U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-254 024

Benzidine Wastewater Treatment Technology

Thomas M. Keinath

Prepared For
Environmental Protection Agency

June 1976

181029

PB 254 024

BENZIDINE: WASTEWATER TREATMENT TECHNOLOGY

prepared by

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for

CRITERIA AND STANDARDS DIVISION
OFFICE OF WATER PLANNING AND STANDARDS
ENVIRONMENTAL PROTECTION AGENCY

June 1976

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NATIONAL TECHNICAL
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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-440/9-76-018

2.

3. R[illegible]NTS ACCESSION NO.
PB254024

4. TITLE AND SUBTITLE
Benzidine: Wastewater Treatment Technology

5. REPORT DATE
Pub. June 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Thomas M. Keinath
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10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
P.O. # WA-6-99-1309-A and
68-01-3390

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Water Planning and Standards
U.S. Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460

13. TYPE OF REPORT AND PERIOD COVERED
Final Report

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
Some editing was performed by EPA

16. ABSTRACT

This report was prepared to provide technologic supporting information for toxic pollutant effluent standards proposed by EPA under Section 307(a) of the Federal Water Pollution Control Act Amendments of 1972. The report identifies potential technologies, assesses implementation feasibility, estimates final effluent characteristics and estimates installation and operation costs for manufacture of benzidine, manufacture of benzidine-based dyes, and applicators of benzidine-based dyes.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Wastewaters Waste Treatment Cost Analysis Cost Comparison Manufacturers	Toxic Pollutant Effluent Standards Federal Water Pollution Control Act	

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT RELEASE UNLIMITED	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES ~~124~~ 122
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE 6.00 - 2.25

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PREFACE

Although many chemicals have been shown to induce cancer in laboratory animals, only a few have been positively identified as human carcinogens. Benzidine and its salts, without question, are carcinogenic to humans.

Carcinogenic hazards to man may result from various types of exposure associated with water. The presence of carcinogens in drinking water, recreational water bodies, food processing waters, or fisheries all are potential sources of human exposure. Ample reason exists, therefore, to believe that the presence of benzidine in the aquatic environment poses a threat to man and the environment.

To secure information relative to (1) the occurrence of benzidine in the wastewaters of synthetic organic chemical manufacturing facilities, (2) the occurrence of benzidine in the wastewaters of benzidine-based dye users, (3) prospects for no aqueous discharge, (4) applicable wastewater treatment technology and (5) to establish the effect of benzidine on publicly owned wastewater treatment facilities, the Environmental Protection Agency contracted Dr. T.M. Keinath to provide appropriate evidentiary material. Such material was gathered, in part, through a questionaire survey and through personal visits to the Buffalo Dye Plant of Allied Chemical Corporation, GAF Corporation, Fabricolor, Inc., Clyde Fabrics, Inc., S. B. Foot Tanning Company, and Peninsular Paper Company.

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SECTION I

EXECUTIVE SUMMARY

(1) At the time of this writing three manufacturers (GAF, Fabricolor, Inc., and Allied Chemical Corporation) produce benzidine-based dyes. Allied Chemical Corporation, however, has announced that it will cease production of such dyes by August 1976. Currently, 1.2 million pounds of benzidine is used in the production of such dyes annually. The Benzidine Task Force of SOCMA has estimated the number of benzidine-based dye applicators at 1200 to 1500.

(2) Housekeeping measures available to the various benzidine manufacturers are adequate to prevent the discharge of benzidine directly to process sewer lines.

(3) Few, if any, process or in-plant changes would result in major benefits with respect to the discharge of benzidine to the waste stream.

(4) Benzidine can be effectively oxidized using the nitrous acid oxidation procedure to end products such as phenolics. Costs for this process were 3.86 and 12.3 cents per pound of product (benzidine) or $69.34 and $46.53 per 1000 gallons of wastewater treated at GAF and Allied Chemical Corporation, respectively. The difference in costs is due to the use of a filtering operation at Allied Chemical Corporation. This technology can be implemented within one year.

(5) Use of ozone for the degradation of benzidine in wastewaters appears to be effective in reducing the concentration to the 1 to 10 ppb level. Considerable additional research and several years are required to fully evaluate the utility of this process. Projected process costs appear excessively high.

(6) Benzidine can be effectively removed from solution to the 1 to 10 ppb level using the adsorption on granular activated carbon procedure. This

technology could probably be implemented within two years after requisite pilot-scale studies have been conducted.

(7) Benzidine at concentrations in excess of 1 ppm is not biologically degraded by the activated sludge process. At the 50 ppb level benzidine is biodegradable. The vast majority (90+%) of benzidine that is removed is biologically degraded while only small quantities (<10%) are incorporated into the sludge mass.

(8) Publically owned wastewater treatment facilities employing the activated sludge process would not be adversely affected if the concentration of benzidine in its influent were maintained at levels less than 1 ppm.

(9) If pretreatment of the wastewater of a benzidine and/or direct dye manufacturing facility was required, it could be accomplished using either the nitrous acid oxidation or activated carbon adsorption methods.

(10) The nitrous acid oxidation procedure for benzidine is the only technology currently employed.

(11) Concentrations of benzidine in the wastewater of a selected dye applicator that represented a "heavy benzidine-based dye use" textile industry situation averaged 13.32 ppb as calculated by the mass balance approach. Actual analyses for benzidine performed on the exhausted dye liquors averaged 3.5 ppb. Similar mass balance analyses conducted for "heavy benzidine-based dye use" leather and paper manufacturing concerns showed calculated residual benzidine concentrations of 0.25 and 8.5 ppb, respectively.

(12) A questionaire survey of three additional textile manufacturers showed that average concentrations of benzidine that could have been present in the wastewater (as calculated by the mass balance approach) ranged from 0.15 to 0.414 ppb. A similar mass balance survey of two leather and five paper manufacturing concerns showed average benzidine concentrations that ranged from 0.27 to 0.73 ppb and 0.0045 to 3.19 ppb, respect-

ively. Corresponding maximum possible benzidine concentrations for the textile, leather, and paper manufacturing concerns surveyed ranged from 0.15 to 0.68 ppb, 0.76 to 1.29 ppb, and 0.02 to 3.19 ppb, respectively.

(13) A tabular summary of treatment technology alternatives has been included as Table II-6.

SECTION II

CHARACTERIZATION OF THE BENZIDINE-BASED DYE MANUFACTURING INDUSTRY

BENZIDINE MANUFACTURE

Production of benzidine-based dyes in the United States is limited to three manufacturing concerns: (1) Allied Chemical Corporation; (2) GAF Corporation; and (3) Fabricolor, Inc. At the Buffalo Dye Plant of Allied Chemical Corporation the benzidine-based dyestuffs are produced as follows: (1) nitrobenzene, the basic raw material, is charged to a closed reactor, where it is reduced to azoxybenzene by caustic in methanol; (2) the azoxybenzene is then transferred to a second vessel where it is mixed with zinc, a solvent, and caustic, resulting in its further reduction of hydrazobenzene; (3) the hydrazobenzene is subsequently transferred to a third reactor where its rearrangement to benzidine sulfate occurs upon the addition of sulfuric acid; (4) the benzidine sulfate is recovered as a slurry after salting by pressure filtration; (5) the benzidine sulfate slurry is then transferred to a closed tetrazotization reactor where acid and sodium nitrite are added; and (6) the benzidine tetrazo is coupled with various chemical constituents to form the dye. It is noteworthy that all transfers between reaction vessels are made through enclosed piping.

Neither GAF Corporation nor Fabricolor, Inc. produce hydrazobenzene as both purchase the material from Lakeway Chemical Company of Muskegon, Michigan. At GAF's Rensselaer Plant the hydrazobenzene is charged to a closed reactor and is subsequently rearranged to benzidine hydrochloride upon the addition of water and muriatic acid. The benzidine hydrochloride is subsequently transferred to a closed tetrazotization chamber through enclosed piping. Upon tetrazotization the tetrazo is coupled with various chemicals to form the dye.

At Fabricolor, Inc. of Paterson, New Jersey the hydrazo is reacted to form benzidine tetrazo which is subsequently filtered and clarified by a closed delivery plate and frame filter press. The tetrazo is then coupled with various chemicals to form the dyestuff.

WASTEWATER SOURCES AND HANDLING PROCEDURES

Due to the known carcinogenicity of benzidine, extraordinary care has been taken in its manufacture in order to reduce its potential contact with workers. As a result, the manufacturing environment has been severely controlled; a condition which is reflected in relatively careful wastewater handling procedures.

Allied Chemical Corporation

Benzidine Sulfate Production ... Because the entire benzidine sulfate production process is enclosed, possible direct discharge of the material is extremely remote. Only the washdown waters from the slurry and salting tanks, the discharge from the pressure filters, the air pollution control scrubber blow-down, the worker clothing laundry wastes, and the floor washdown waters would likely contain benzidine. These waters are collected either in a decontamination reaction vessel or in a sump. All floor washings, furthermore, are directed to the sump. The waters collected there are subsequently transferred to the decontamination vessel for treatment by the nitrous acid oxidation procedure. Virtually no opportunity exists for the discharge, either accidental or otherwise, of untreated benzidine sulfate to the process sewer.

Dye Production ... After tetrazotization the tetrazo is coupled with various chemicals in enclosed reactors to form the dye. Although the dye product is certified to contain no more than 20 ppm of benzidine, it is usually assayed in the 10 to 13 ppm range. Since complete chemical conversion is not achieved in the dye production reaction, trace quantities of benzidine would also likely be contained in the dye mother liquors that are discharged from the dye filter presses to the process sewer. Dye production waste mother liquors and equipment and operations area wash waters are not treated by the nitrous acid procedure prior to discharge to the process sewer.

GAF Corporation

Benzidine Hydrochloride Production ... Since benzidine is not salted-out and is not pressure filtered at GAF, no opportunity for the discharge of benzidine from those unit processes exists. Only the air pollution control scrubber blowdown, the worker shower wastes, and the floor washdown waters could possibly contain benzidine. These waters are collected in a sump which also serves as a decontamination reaction vessel. The waters collected there are subsequently subjected to decontamination by the nitrous acid oxidation procedure.

Dye Production ... As in the case of Allied Chemical Company, trace benzidine concentrations are likely contained in the dye production wastewaters at GAF. At GAF, however, only the waste dye mother liquors are not treated by the nitrous acid procedure prior to discharge to the process sewer.

Fabricolor, Inc.

The primary source of benzidine which could potentially be discharged to the process sewer of Fabricolor, Inc. is the discharge of the filter press which is employed to filter and clarify the benzidine tetrazo. After filtering a batch of the tetrazo, the material is transferred via a closed system to a coupling vessel. After transfer, the filter press is washed with water while closed. The washings are also transferred to the coupling vessel. Subsequently a bleach solution is introduced to the filter press. This decontamination solution is then discharged to the process sewer. The press is then opened and the solid residue is removed and transported to a landfill.

The benzidine-based dye mother liquors constitute a secondary source of benzidine that could be discharged to the process sewer at Fabricolor, Inc. Like the other two manufacturers of benzidine-based dyes, Fabricolor discharges the mother liquors directly to the process sewer.

At Fabricolor, Inc. no provision has been made for the treatment of floor washdown and air scrubber waters. It is noteworthy, furthermore, that Fabricolor, Inc. has no worker showers which could potentially be a source of benzidine that could be discharged into the wastewater stream.

Housekeeping Practices

Due to the long-term recognition of the carcinogenicity of benzidine and the recent implementation of the Occupational Safety and Health Act, the housekeeping practices employed by benzidine sulfate (chloride) manufacturers are extremely stringent. (As an example, Allied Chemical Corporation's operating, maintenance, and control practices related to the industrial hygiene program for benzidine have been include as Appendix A.) Accordingly, one can conclude with relative assurance that no in-plant or production process changes would result in major benefits with respect to the discharge of benzidine to the wastewater stream.

WASTEWATER VOLUMES AND CHARACTERISTICS

Allied Chemical Corporation

At Allied Chemical Company's manufacturing facility approximately 2.64 million gallons (22 million pounds) of wastewater is discharged annually due to the production of benzidine at a production level of one million pounds expressedas benzidine sulfate. This represents approximately seven to eight-tenths of one-percent of the total wastewater flow (370 million gallons). One analysis for benzidine has been conducted on the benzidine production process wastewaters prior to decontamination by the nitrous acid oxidation procedure. This analysis showed a concentration of benzidine of 963 ppm. Allied produces approximately 4.4 million pounds of benzidine-based dyes annually.

Benzidine concentration levels contained in the dye production wastewaters at Allied's Buffalo Dye Plant have been recorded in Table II-1 for fourteen dye mother liquor samples obtained from the dye filter press exhausts during 1974. Half of the fourteen samples showed less than detectable levels of benzidine while the others showed levels that ranged from 30 to 115 ppb.

If one assumed that those samples that contained less than detectable levels actually contained 10 ppb, then an average concentration of benzidine of 33.7 ppb can be calculated for the data presented. Assuming an average daily dye production of 16,200 pounds and an average mother liquor discharge of 84,000 pounds, one can estimate an expected average daily mass discharge of benzidine of approximately 2.8×10^{-3} pounds in the dye production wastewaters.

As noted earlier, the discharge from the nitrous acid treatment process is sewered and thence diluted with other manufacturing wastewaters at the Buffalo Dye Plant which contain, in addition to the usual dye and pigment manufacture wastes, wastewaters from solutions used to clean equipment, wastes from dye intermediate manufacture and from the manufacture of organic specialties such as dimethyl aniline, diethyl aniline, resin chemicals and special acid anhydrides. The detectability limit for benzidine in the diluted matrix is 2 - 5 ppb using the chloramine-T procedure.

Results of analyses performed on the combined wastewater flow from Allied's Buffalo Dye Plant during the period which extends from 24 March to 31 May 1974 have been summarized in Table II-2. All analyses were performed on 24-hour composite samples collected at 0800 hours at the influent to the pretreatment works. During the period of analysis, benzidine was manufactured at approximately rated capacity and the nitrous acid treatment performance was deemed to be operating at best attainable efficiency. It is noteworthy, however, that on 31 March 1974

TABLE II-1

Benzidine* Contained in Dye Mother Liquors

Date	Dye Type	Lbs. Dye Per Batch	Lbs. Waste Per Batch	Benzidine Conc. (ppb)
3-21-74	Erie Fast Red FD	1150	18,000	64
3-26-74	Erie Catchine 3G	1300	16,000	<10
3-27-74	Erie Black GX00	16,600	73,000	<10
3-28-74	Milling Scarlet	1000	15,000	<10
3-28-74	Erie Orange 2R	1730	13,000	50
3-28-74	Erie Brown 3GN	8600	34,000	<10
4-25-74	Erie Green GPD	2500	68,000	63
5-16-74	Erie Scarlet B	700	10,000	115
7-29-74	Erie Black GX00	16,600	73,000	30
7-30-74	Erie Black GX00	16,600	73,000	<10
7-31-74	Erie Black GX00	16,600	73,000	30
8-1-74	Erie Black GX00	16,600	73,000	<10
8-2-74	Erie Black GX00	16,600	73,000	<10
8-8-74	Lanamid Golden Brown	1800	-	50

* Level of Detectability = 10 ppb.

TABLE II-2

Benzidine in Combined Wastewaters of Allied's Buffalo Dye Plant

Date	WW/Flow (10^6 lbs/day)	Benzidine Conc. (ppb)	Benzidine Loading (lbs/day)
3-24-74	10.4	110	1.1
3-28-74	12.9	30	0.3
4-1-74	11.5	650	5.2
4-5-74	10.9	190	2.2
4-9-74	12.7	*	-
4-13-74	10.1	80	0.8
4-17-74	12.9	30	0.4
4-21-74	10.8	70	0.8
4-25-74	13.0	100	0.1
4-29-74	13.1	120	0.2
5-3-74	11.2	50	0.6
5-7-74	10.1	*	-
5-11-74	13.6	10	0.2
5-19-74	8.7	*	-
5-27-74	8.4	20	0.2
5-31-74	11.1	50	0.5

Note: * indicates a concentration $<$ 2 - 5 ppb approximately one to two pounds of benzidine were washed directly to the process sewer system when the Vallez filter in Building 54 developed a leak. This was reflected in high loadings on 1 & 2 April.

The data shown in Table II-2 was analyzed statistically (II-3) in two ways: including (Mode 1) each of the 16 data points assuming that the three samples that showed less than detectable concentration had concentrations of 5.0 ppb, and excluding (Mode 2) those values which fall outside the high 99% confidence limit the analysis showed the following were loadings in pounds per day. The data point for 1 April (a high value which is attributable to a preventable occurrence).

	Mode 1	Mode 2
Average	0.80	0.38
Std. Deviation	1.30	0.33
High 95% Conf.	1.49	0.57
High 99% Conf.	1.75	0.65

Comparison of the total average daily quantity of benzidine discharged in the combined wastewater stream (0.38 pounds) with the sum of the daily contribution of benzidine from the two primary sources (0.0036) shows that 99 percent of the benzidine that appears in the combined wastewater flow cannot be accounted for through an analysis of the point source contributions (dye manufacture wastes and nitrous acid treated effluents). The most plausible explanation for this anomaly is that benzidine-based dyes or other benzidine derivatives are reduced in-situ to benzidine in the process sewers.

GAF Corporation

Because GAF does not filter benzidine dihydrochloride, only the air pollution control scrubber blow-down, worker shower wastes, floor washdown waters and dye mother liquors are ultimately discharged from the benzidine-based dye manufacturing building. The volume of discharge from the first three sources is approximately 78,000 gallons (650,000 pounds) annually. This represents approximately 7.8 thousanths of one-percent of the total wastewater flow (1 billion gallons) or 18.5 thousanths of one-percent of the process water flow (421 million gallons) at the Rensselaer Plant. No analyses for benzidine have been conducted on the process wastewaters prior to decontamination by the nitrous acid oxidation procedure. GAF annually produces 140,000 pounds of benzidine and 1.2 million pounds of benzidine-based dyes.

Benzidine concentration levels contained in the discharge from the building in which the benzidine and benzidine-based dyes are produced (600,000 gallons per day average flow) were determined to be less than detectable (detectability limit = 5 ppb) in 45 of 52 daily composite samples. This corresponds to mass discharges of less than 0.025 pounds per day. Concentrations of benzidine in the remaining seven samples ranged from 12 to 134 ppb and averaged 50 ppb.

Results of 84 of 89 analyses for benzidine performed on composite samples of the combined wastewater flow from the GAF plant at Rensselaer showed concentration levels less than the level of detectability (1.0 ppb). This corresponds to mass discharges of less than 0.037 pounds per day from the Rensselaer facility. Of the five that contained detectable benzidine, three had concentrations less than 5 ppb, one had a concentration of 26 ppb, and the other a concentration of 42 ppb.

Fabricolor, Inc.

Total wastewater flows at Fabricolor, Inc. average approximately 15.5 million gallons (129 million pounds) annually which derives from an average daily flow rate of 50,000 gallons/day over a 6-day work-week. Fabricolor produces benzidine dyes batchwise, one batch per day, two days per week. Manufacturing effluents associated with the production of a batch include 360 gallons (3000 pounds) of aqueous wastes from the filter press wash and 6950 gallons (58,000 pounds) of filtrate water. Analyses performed for Fabricolor, Inc. by International Hydronics, Inc. on a grab sample of these waste streams showed concentrations of benzidine of 16 and 72 ppb, respectively, as determined by the Chloramine T procedure. Moreover, the air scrubber blow-down which contributes 180 gallons (1500 pounds) of water per batch was assayed at 24 ppb of benzidine. The total discharge of benzidine on days during which benzidine-based dyes were manufactured was thus calculated to be 4.26×10^{-3} pounds per day. If averaged over the total daily discharge, a concentration level of 10.2 ppb of benzidine could be anticipated.

Results of analyses performed on a 24-hour composite sample of the total process wastewater stream are as follows:

pH	2.9
Turbidity	1700 JTU
Total Solids	14,656 ppm
Suspended Solids	124 ppm
Volatile Solids	1031 ppm
Volatile Suspended Solids	87 ppm
COD	1000 ppm
BOD_5	175 ppm
TOC	300 ppm
Cobalt	0.4 ppm
Copper	1.83 ppm
Chromium, hexavalent	0.01 ppm
Chromium, trivalent	0.12 ppm

Fabricolor annually produces 60,000 pounds of benzidine and 0.5 million pounds of benzidine-based dyes.

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SECTION III

BENZIDINE: WASTEWATER TREATMENT TECHNOLOGY

TREATMENT TECHNOLOGY ALTERNATIVES

Development of treatment technology for the destruction or removal of benzidine from wastewaters has occurred only recently, certainly not more than a decade ago. Various treatment procedures that have been proposed as potentially feasible methods include destruction using ionizing (gamma) radiation, oxidation using ozone, hydrogen peroxide, or nitrous acid, adsorption on granular activated carbon, and biodegradation using the activated sludge process. Neither the ionizing radiation nor the oxidation procedure using hydrogen peroxide have, to the knowledge of the author, been evaluated directly using the carcinogen, benzidine. Only the oxidation procedure using nitrous acid has been implemented at plant scale by two of the three benzidine dye manufacturers (Allied Chemical Corporation & GAF Corporation) and only for treating benzidine manufacture wastewater.

OXIDATION WITH NITROUS ACID

Chemical Reactions

Reaction of benzidine with excess nitrous acid in a strong acid medium yields the benzidine tetrazonium salt. The reaction has been observed by Dien (III-1) to be practically quantitative. Further, little or no benzidine can be detected in the completed reaction mass. The benzidine tetrazonium salt, however, is not stable. It has been noted by Dien to decompose slowly and spontaneously at ambient temperatures and very readily at higher temperatures. The decomposition products in acidic medium include phenyl phenol, diphenyl dichloride, dihydroxybiphenyl, and hydroxychlorobiphenyl as major constituents and phenol and biphenylphenol as minor constituents. No benzidine and no polychlorinated biphenyls other than dichlorobiphenyl can be detected in the acid decomposed product.

In an alkali medium, the benzidine tetrazonium salt also decomposes with the evolution of nitrogen gas. The product is a highly colored material which probably is an azo compound which is formed when the decomposed phenolic product acts as a coupler and reacts with the tetrazonium salt. Under oxidizing conditions, these azo compounds as well as the benzidine tetrazonium salt can be expected to degrade to di-pheno quinone. Only under strong or catalytic reducing conditions would the possibility exist, that these azo compounds could revert back to benzidine itself.

A process schematic diagram has been provided by the Task Force on Benzidine of the Synthetic Organic Chemicals Manufacturing Association (SOCMA). The diagram has been labeled as Figure III-1 and has been included herein.

Waste Collection Systems

Allied Chemical Corporation ... The nitrous acid treatment method has been implemented at the Buffalo Dye Plant of Allied Chemical Corporation. At that location (see Figure III-1) the filtrate and/or wastes from the Vallez filter flow directly into the rubber lined, agitated, 3000 gallon treatment reactor. Drainage from the product sampling box is directed into the holding tank which feeds the treatment reactor. Drainage from the process scrubber is routed directly to the treatment reactor. All other process wastes including the discharges of the locker room shower and laundry washing machine are directed from the floor drains to the double sump on the first floor of Building 54. These wastes are subsequently pumped from the sump via pumps to the holding tank. One pump is employed as the primary pump while the other serves as a spare being activated by a high level switch in the sump.

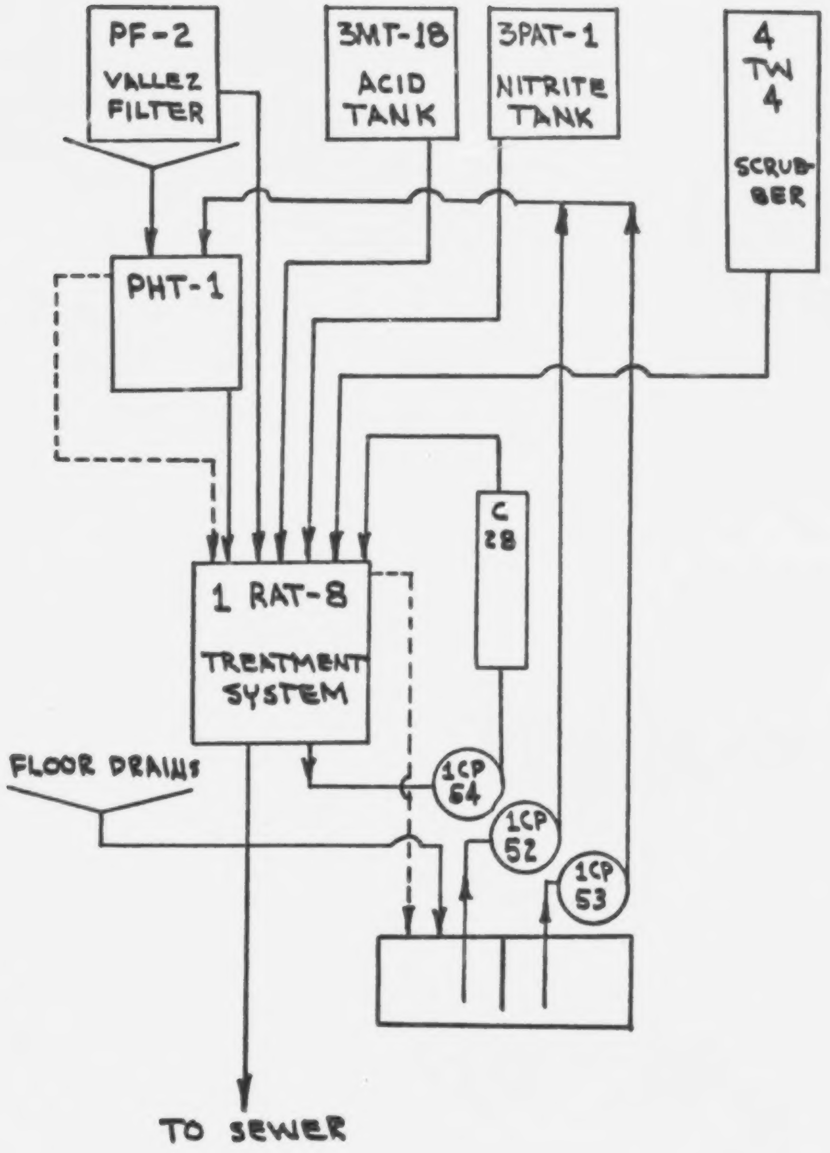


FIGURE III-1

Process Flow Sheet For

Acid Nitrite Decomposition of Benzidine

GAF Corporation ... Also using the nitrous acid oxidation procedure GAF discharges all floor washings, shower and change room discharges, and the blowdown of the caustic scrubber into a 5000 gallon catch tank. A schematic diagram of the system is shown in Figure III-2. When approximately 3000 gallons of wastewater has been collected (ca. 2 weeks elapsed time) the nitrous acid oxidation process is initiated. After treatment, the contents of the catch tank are discharged to the process sewer.

Nitrous Acid Treatment Process

Allied Chemical Corporation ... When approximately 2500 gallons of process and wash-down wastewaters have been collected in the treatment reactor the following batch treatment procedure is initiated (refer to Figure III-1):

(1) Fill H_2SO_4 measuring tank (3-MT-18).

(2) Mix 20% $NaNO_2$ solution in 3-PAT-1.

(3) Transfer filtrate from Vallez pressure filter (PF-2) to RAT-8 along with the first wash from PF-2 to RAT-8 to total volume of 2500 gallons (20,850 pounds).

(4) Circulate the contents of RAT-8 through the cooler (C-28) using a pump (1 CP-54) until the temperature of the contents of RAT-8 has been reduced to 10° C.

(5) Add H_2SO_4 from 3-MT-18 to RAT-8 as necessary to hold contents of RAT-8 acid to Congo Red indicator paper (pH = 2.0).

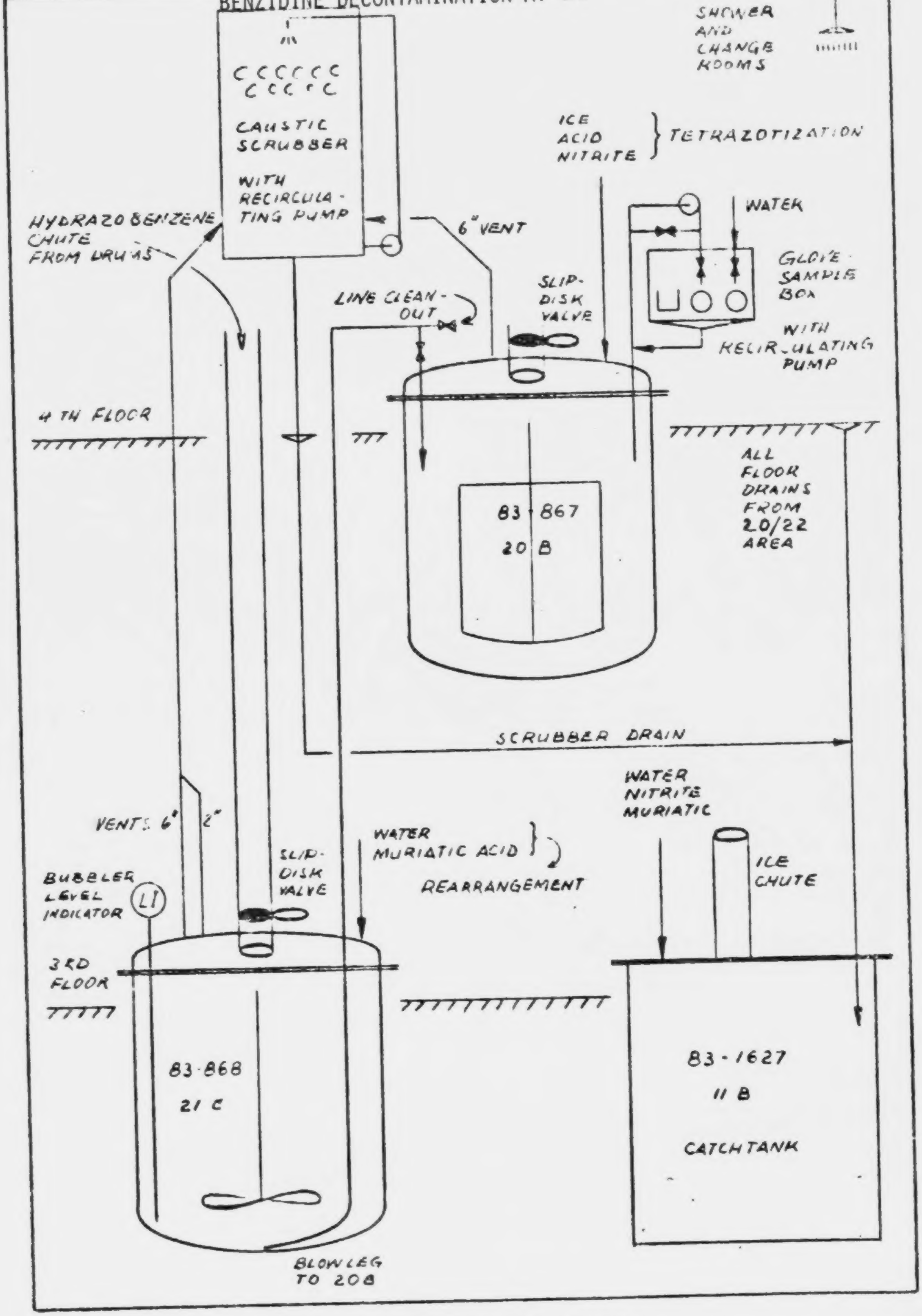
(6) Slowly transfer the 20 percent sodium nitrite solution from 3-PAT-1 to RAT-8. Sample and check with starch-iodide at 15-minute intervals. When the test shows the presence of nitrite after 30 minutes, the contents of RAT-8 are drained to the process waste treatment sewer, where it undergoes dilution and further treatment (pretreatment) which consists of equilization, neutralization, and clarification prior to discharge to the municipal sewer.

(7) The above procedure is repeated for the balance of the washes from PF-2.

(8) The above procedure is repeated for the treatment of accumulated liquids from drains which collect in PHT-1 after transferring contents of PHT-1 to RAT-8.

FIGURE III-2

BENZIDINE DECONTAMINATION AT GAF



BUILDING B3 - BENZIDINE DYE MANUFACTURE

NO PERSONNEL CONTACT - ZERO EXPOSURE - CLOSED LOOP SYSTEM

8-26-75 KB PPE

Tandem air-operated valves are used on the inlet and drain lines of the treatment reactor. Air piping to these valves is arranged such that both are operated by a single cock. In this manner the inlet valve is closed when the drain valve is open and visa versa. This system prevents the introduction of untreated effluent to the treatment reactor while the drain valve is open.

The treatment system is rated at five charges per day. Currently approximately three batches are processed per day.

GAF Corporation ... Essentially the same procedure is employed by the GAF Corporation with the exception that muriatic acid is used in place of sulfuric acid. Also, the temperature is reduced to 10°C using ice rather than a cooler. In all other respects the chemical treatment procedure is identical.

Although the batch treatment process at GAF could accommodate three to five charges per day, at current production levels only one batch of 3000 gallons is treated bi-weekly.

Nitrous Acid Treatment Process Performance

Allied Chemical Corporation has conducted analyses for benzidine on samples of wastewaters treated using the nitrous acid oxidation procedure. Results of such analyses have been tabulated in Table III-1. Of the eleven samples analyzed, nine showed concentrations less than the detectable level (10 ppb; refer to Appendix B) while two showed concentrations of 190 and 218 ppb.

If one were to assume that the average concentration of benzidine in the nitrous acid treated matrix was 10 ppb, then one would expect that approximately 8×10^{-4} pounds of benzidine would be discharged daily along with an average of 9700 gallons of nitrous acid treated effluent at the Buffalo Dye Plant.

GAF has also conducted analyses on the nitrous acid treated effluent. Because the procedure they used for the chloramine-T method for benzidine lacked sensitivity (detectability limit of 10 to 20 ppb), all of their results showed

TABLE III-1

Benzidine* Contained in Nitrous Acid Treated Wastes

Date	Type of WW Treated	pH	Benzidine Conc. (ppb)
8-21-74	Filter Press Filtrate	2.2	190
8-30-74	Filter Press Filtrate	1.5	<10
8-30-74	Filter Press Filtrate	1.5	<10
8-30-74	Filter Press Filtrate	1.6	<10
8-30-74	Filter Press Wash Water	1.5	<10
9-1-74	Filter Press Filtrate	2.1	218
9-3-74	Filter Press Wash Water	1.6	<10
9-1-74	Filter Press Wash Water	4.2	<10
9-1-74	Filter Press Wash Water	4.0	<10
9-5-74	Filter Press Wash Water	2.4	<10
9-7-74	Filter Press Wash Water	1.9	<10

* Level of Detectability = 10 ppb.

non-detectable levels of benzidine. Nonetheless, their results partially, but not conclusively, confirmed the results obtained by Allied.

As above, if one were to assume that the concentration of benzidine in the nitrous acid treated matrix was 10 ppb, then one would expect that approximately 2.5×10^{-5} pounds of benzidine would be discharged daily with an average of 300 gallons of nitrous acid treated effluent at GAF's Rennsselaer Plant.

Nitrous Acid Treatment Costs

Allied Chemical Corporation ... Capital construction and operation and maintenance costs have been estimated for the nitrous acid oxidation method by the Benzidine Task Force of SOCMA. The capital costs (1969 index) have been detailed as follows for the Buffalo Dye Plant:

	Cost ($)	
Description of Element	Material	Labor
Nitrite Dissolution & Distribution System	5400	4300
Acid Distribution Piping	3000	3500
pH and Sample Controls at RAT-8	1200	1200
Acid Sump Pump (CP-52 and Piping to PHT-1)	5200	2800
Holding Tank (PHT-1)	2300	1400
Pump (CP-54) for Circulation	6000	3800
Graphite Cooler (C-28)	15,500	5000
Sewer Revisions	400	800
Decontamination	-	300
Construction Overhead	15,000	-
Engineering	13,600	-
Totals	67,600	23,100
TOTAL CAPITAL COSTS	$90,700	

Moreover, it has been estimated that the annual costs for O&M are $108,000 (III-4). Assuming that the capital is amortized at 10 percent over a 10-year period, then the annual capital costs are calculated to be $14,745. The total annual costs then are $122,745 for the system which has been installed at the Buffalo Dye Plant of the Allied Chemcial Corporation.

A total of one million pounds of benzidine sulfate expressed as benzidine is produced by Allied Chemical Corporation annually. Associated with this level of production, a total of 2,637,900 gallons of wastewater is produced annually. Expressing the cost of using the nitrous acid process to oxidize the benzidine in the wastewater on a unit cost basis one determines that the cost per 1000 gallons of wastewater treated is $46.53 while the cost expressed on a per pound of product (benzidine sulfate) basis is equivalent to 12.3 cents.

GAF Corporation ... A complete breakout of the capital cost elements associated with the construction of the nitrous acid treatment process at the Rensselaer plant is not available. Nonetheless, the total capital cost of the system was estimated at $3000 (1965 index) and the operating cost was estimated at approximately $5000 per annum (III-3). Assuming that the capital is amortized at 10 percent over a 10-year period, then the annual capital costs are calculated to be $409. The total annual costs for the system which has been installed by GAF Corporation then are $5409.

Since GAF's annual discharge is 78,000 gallons, the unit costs for the nitrous acid treatment system is $69.34 per 1000 gallons of wastewater treated. Expressed on a per pound of product (benzidine; 140,000 pounds annual) basis the cost is equivalent to 3.86 cents.

Comments ... Although the unit costs on a per 1000 gallon basis appear high in contrast to cost figures for the treatment of other industrial wastewaters, the total annual costs are not prohibitive for Allied Chemical Corporation and

GAF Corporation. The unit costs are high primarily because extensive water conservation measures are practiced by these two manufacturers.

The unit costs on a per pound of product basis incurred by Allied are higher by a factor of 3.6 than those incurred by GAF. This is due to the fact that Allied's Buffalo Dye Plant uses a Vallez filter to filter the benzidine sulfate whereas GAF uses no such filter. The filtering operation is the source of the majority of the benzidine production process wastewater which averages 2.64 gallons per pound of benzidine produced at the Buffalo Dye Plant. In contrast, GAF uses approximately 0.5 gallons of water per pound of product.

OXIDATION WITH OZONE

Studies pertaining to the use of ozone for the purpose of oxidizing benzidine to innocuous end products have been confined to the laboratory to date. Three such laboratory bench-scale studies were conducted either by or under contract to Allied Chemical Corporation and have been reported by the Benzidine Task Force of SOCMA. (III-5)

Results of Laboratory Studies

The first of the three batch studies was conducted using a distilled water matrix spiked with 117 ppm benzidine. Using a glass bubbler system through which ozone was applied at the rate of 0.605 liters per minute to four liters of the sample, the following results were obtained:

Time (min.)	Ozone Absorbed (ppm)	% Ozone Absorbed	Residual Benzidine (ppm)
0	0	0	117
3	51	38.3	103
6	80	30.2	63
12	115	21.9	19
18	-	-	1
24	170	15.9	0.09
36	219	13.9	0.01

Qualitatively it was noted that originally the solution was clear, then turned to a light brown color, then to dark brown, then to a yellow color, and finally to a faint yellow. From the data, it was concluded that ozone effectively oxidized benzidine and its intermediates.

Subsequently, a study was conducted using benzidine spiked samples of the effluent of the Pretreatment Works of Allied's Buffalo Dye Plant. One sample was analyzed as a blank while four samples were ozonated for various periods to residual ozone concentration levels of 240, 495, 715, and 950 ppm. These were subsequently subjected to analysis. Results of this study are tabulated as:

Parameter	Ozone Concentration (ppm)				
	0	248	295	715	950
Benzidine (ppb)	207	1	1	-	-
COD (ppm)	514	-	375	356	336
TOC (ppm)	313	290	201	140	166
Oil & Grease (ppm)	3.4	2.4	0.8	0.6	0.4
NH_3 (ppm)	27	23	24	24	26
SS (ppm)	25	52	71	85	116
pH	8.0	6.4	5.2	5.4	5.5
Color	2000	200	40	40	40

One can observe that ozone very effectively oxidized benzidine and reduced the concentration of several other parameters. It is noteworthy, furthermore, that the pH decreased for higher ozone dosages. This is likely due to the fact that ozone attacks double bonds in organic compounds and usually forms different organic acids because of the oxygen replacement of the carbon-carbon double bond.

Although the preliminary laboratory studies were positive regarding the oxidation of benzidine, it is important to point out that many important questions remain unanswered. For example: (1) what effect do other organics normally found in the wastewater have on the ozone dosage requirements and on the kinetics of oxidation? (2) what are the by-products of the oxidation? These, as well as several other unknowns, must be elucidated before the technical feasibility of employing ozone for the oxidation of benzidine can truly be established.

At this time, ozonation cannot be regarded as a viable treatment alternative for benzidine due to an inadequate data base.

Projected Process Costs

Based on the preliminary laboratory studies, order-of-magnitude process cost projections have been made (III-5). Assuming that ozone would have to be applied at a dosage of 500 ppm to achieve the desired reductions in benzidine in the effluent of Allied's Buffalo Dye Plant, the daily ozone requirement is projected at 25,000 pounds. This would require a capital expenditure for ozonation equipment of approximately 3.8 million dollars. The installed cost would logically be twice the equipment cost.

Annual operating expenses for maintaining such an ozonation system have been estimated (III-5) as follows:

Electrical Power @ $0.02/kwh	$ 890,000
Oxygen @ $0.025/lb.	365,000
Depreciation @ 10% of capital	750,000
Maintenance @ 5% of capital	350,000
Taxes, insurance, etc. @ 1.5% of capital	100,000
Labor (1 man/shift)	40,000
TOTAL	$2,495,000

While these projections give an order-of-magnitude estimate of the costs which would be incurred, realistic cost estimates could only be made after extensive laboratory-and pilot-scale studies have been conducted. These would unequivocably establish the ozone consumption requirements. Such studies would likely require a one to three-year study period. They could potentially show an ozone consumption rate of one-quarter to twice that used for the cost analysis given above. Obviously, this could dramatically affect the costs for implementing the ozonation process; either upward or downward.

ADSORPTION WITH GRANULAR ACTIVATED CARBON

Although the adsorption process was known in ancient times, it was not until the 20th century that powdered carbon was used on a large scale for the removal of taste-and-odor-causing constituents from potable waters. Subsequent development of granular activated carbons during the 1930's led to the expanded use of active carbon; for sugar decolorization, solvent recovery, and liquid and gas purification during the late 1940's. As part of the Advanced Waste Treatment Program (1960's) of the Federal Water Pollution Control Administration (FWPCA) the adsorption process was shown to be technically sound and economically attractive for the removal of refractory and toxic dissolved organics from wastewaters.

As early as 1951 evidence exists in the literature relative to the removal of certain toxicants and carcinogens from solution using activated carbons (III-6, III-7, & III-8). The first experimental data which showed that benzidine itself could be effectively removed from wastewaters using granular activated carbon was provided by Sterbacek, Tausk, and Trca (III-9). Recently, Hager and Rizzo (III-10) conducted a broad spectrum adsorption isotherm study on many organic toxicants and concluded that the compounds selected could probably be effectively removed from water by adsorption. In all cases preliminary evidence indicated that the adsorption process could potentially be employed to treat a wastewater to the extent that it would meet the EPA effluent objectives for toxic chemicals studied.

Process Design Parameters

Design of any adsorption system requires specification both of adsorption equilibria and kinetics. A laboratory adsorption isotherm testing procedure (adsorption equilibria) is a reliable technique to ascertain the technical feasibility of treatment using granular activated carbon. This testing procedure specifically estimates:

(1) The probable effluent levels of contaminant concentration obtainable by adsorption treatment.

(2) The weight of contaminant that will be adsorbed by the adsorbent at the contaminant concentrations studied.

A cursory, three-point adsorption isotherm conducted by the Benzidine Task Force of SOCMA (III-11) using Filtrasorb 300 (a product of Calgon Corp.) showed adsorption capacities for benzidine of 7.1, 4.22, and 2.19 percent by weight for equilibrium aqueous-phase concentrations of benzidine of 14,900, 900, and 10 micrograms per liter, respectively. This data has been plotted in Figures III-3 and III-4 along with comparable data reported by Hager and Rizzo (III-10) for DDD, DDT, DDE, and two isomers of the PCB family. Generally, the data shows that benzidine adsorbed better than the five other toxicants. Only for the higher solution-phase concentrations (greater than 10 micrograms per liter) did DDD and Arochlor 1242 (a PCB isomer) adsorb better than benzidine. Based on the isotherm data presented, it appears that adsorption on granular activated carbon is a technically feasible process for removing benzidine from wastewaters. It should be cautioned, however, that the data base is extremely sketchy.

Two additional considerations relating to the isotherms are worthy of mention. First, because of the limitations of the Chloramine-T procedure for benzidine, residual solution concentrations of less than 5 ppb cannot be determined. Consequently, the isotherm for benzidine was extrapolated (dashed line) for concentrations less than 5 ppb. Based on the isotherms presented by Hager and Rizzo (III-10) and a thorough knowledge of the adsorption process, the actual benzidine isotherm in this range of concentrations (1 to 5 ppb) would be expected to closely approximate that which was extrapolated.

ADSORPTION ISOTHERMS FOR DDD, DDT, DDE AND BENZIDINE

FIGURE III-3

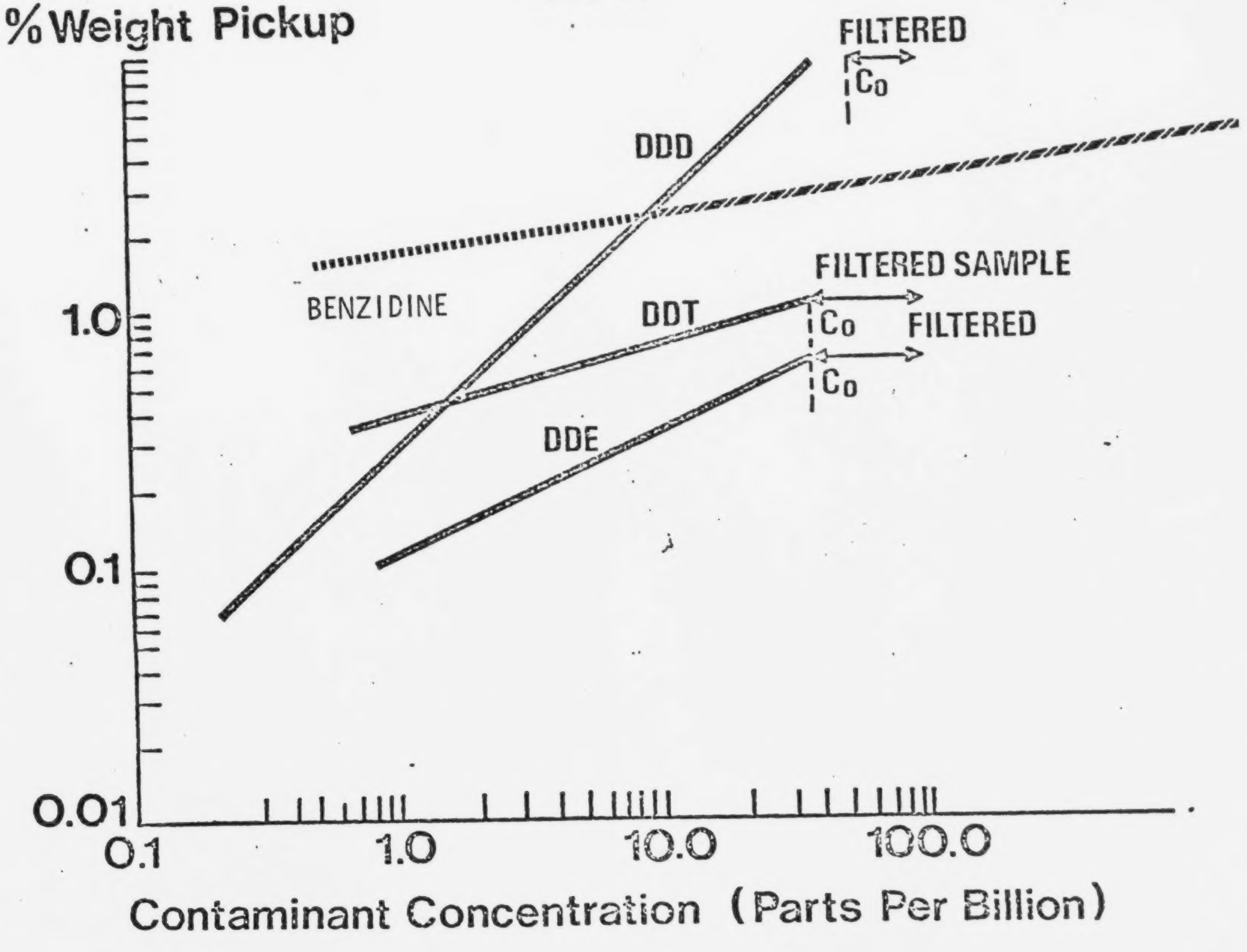
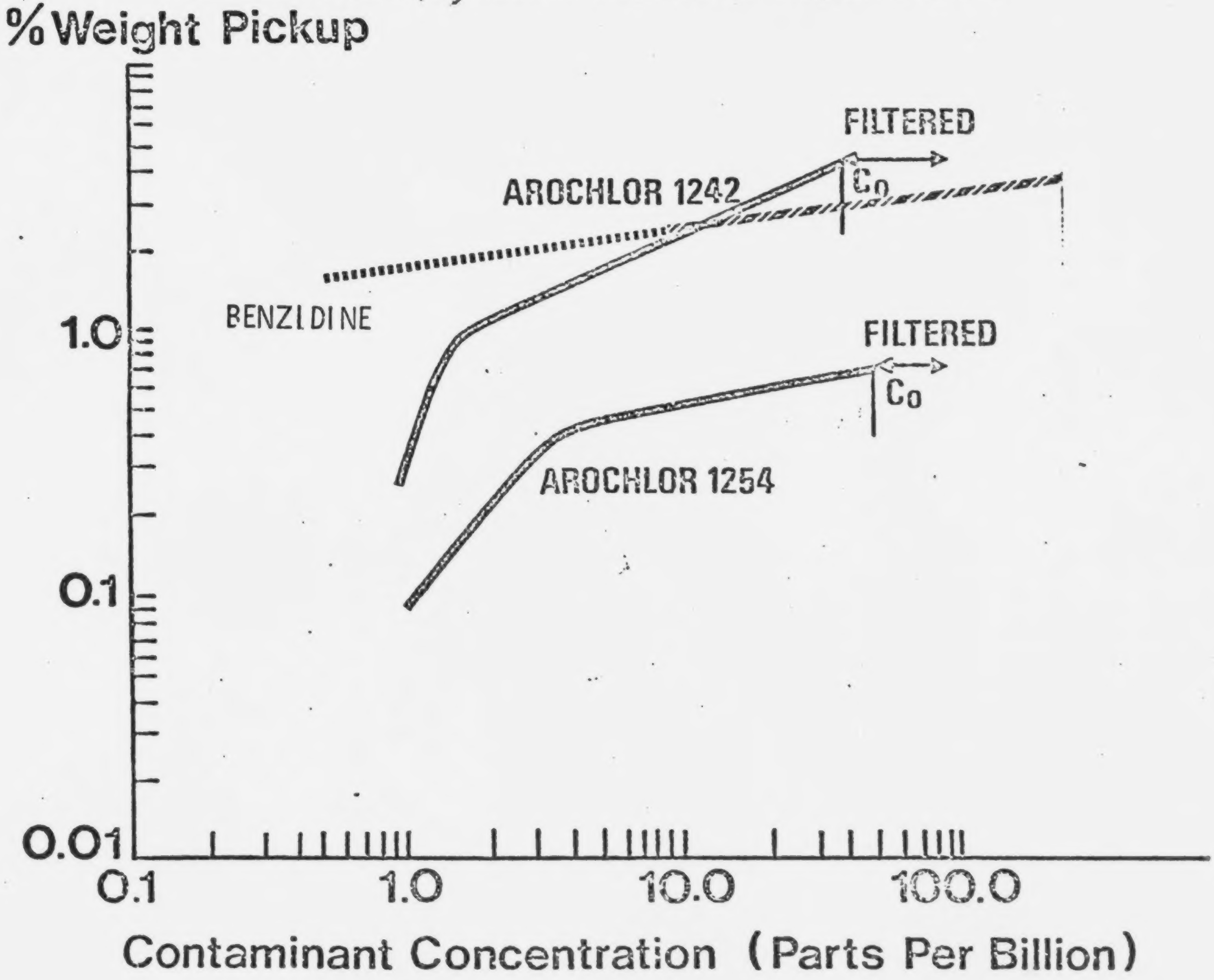


FIGURE III-4

ADSORPTION ISOTHERMS FOR AROCHLOR 1242, AROCHLOR 1254, AND BENZIDINE



Secondly, the solubility of benzidine sulfate is approximately 80 mg/l (III-11). Consequently, if benzidine sulfate were present in the wastewater at concentrations in excess of that level, then the excess could readily be removed through diatomaceous earth (DE) filtration. In such cases a DE filtration system would preceed the activated carbon contactor.

Specification of the kinetics or rates of adsorption cannot usually be achieved in the laboratory. Determination of the contact time required (for granular carbon beds) to effect desired reductions in benzidine concentration on a wastewater would usually be performed in small pilot carbon beds under dynamic hydraulic flow conditions. This is a well-established procedure which serves to determine the number of contactors, the activated carbon inventory, and the actual contact time required for a prototype installation. Whereas the isotherm data serves to establish the technical feasibility of the adsorption process, pilot-scale information is required to establish the economic feasibility of employing the adsorption process for any specific application. No pilot-scale studies have to date been conducted on a wastewater which contains benzidine. Consequently, prototype process economics cannot be directly established, but can only be indirectly approximated through analysis of the economics of existing adsorption installations.

Requisite pilot-scale studies and more comprehensive isotherm studies could logically be completed during a one-year study period. Upon completion of such a study, the adsorption technology could likely be implemented within one to two years. It is imperative to note, however, that such studies must be completed before management decisions regarding the adsorption process can be made.

Process Configuration and Operation

An adsorption installation which could be employed for removing benzidine from wastewaters would likely consist of the following process elements: (1) a diatamaceous earth filtration system; (2) a series of activated carbon contactors; (3) a carbon reactivation furnace; and (4) a carbon-water transport system. As was indicated above, a DE filtration system would be installed if benzidine sulfate were present in the wastewater at concentrations in excess of 80 mg/l, the solubility limit. This unit process would be installed in advance of the carbon contactor in the process stream. It would serve to remove any particulate benzidine sulfate from the waste stream allowing only the soluble benzidine to pass on to the carbon contactors. It was shown earlier that the soluble benzidine can probably be removed from the waste stream through adsorption on granular activated carbon.

The adsorbers contain the granular activated carbon beds through which the wastewater flows. They can be designed either for pressure or gravity flow to achieve the desired contact time of the water with the carbon. Flow rates usually are under 10 gallons per minute per square foot of carbon bed surface area. Contact times for industrial wastewater mixtures usually are in excess of 60 minutes -- approximately twice the time employed for the purification of domestic or municipal wastewaters.

All carbon contactors are usually fitted with well-designed water distribution-underdrain systems to ensure efficient backwashing of the bed as well as even distribution of the influent wastewater over the entire cross-section of the bed. Established filtration design practices are usually employed in the design of carbon adsorption contactors. It is to be noted, however, that carbon beds must periodically be removed via a water slurry and that special provisions must be made for the removal and transport of the carbon such that the procedure is not a hazard to workers.

Carbon beds are normally in excess of 10 feet in depth and usually are of one of five basic configurations: (1) moving beds; (2) beds in series; (3) beds in parallel; (4) expanded beds; and (5) packed beds. The type of configuration selected depends on a number of variables including the total water flow, concentration of suspended solids, and degree of contaminant reduction desired. Although the final design of any system must be predicated on dynamic pilot-scale studies, it is anticipated that a packed-beds-in-series configuration would prove most effective for removing benzidine from wastewaters.

Thermal oxidation is employed to reactivate the exhausted carbon for re-use. Further, multiple hearth furnaces or rotary kilns are employed for reactivation of the exhausted carbon. The size of the thermal reactivation equipment is based on the exhaustion rate; i.e., the weight of carbon exhausted per thousand gallons of wastewater treated and the weight of the contaminant on the carbon. Excess capacity is always designed into the thermal reactivation unit to allow for variances in carbon use rate due to changes in wastewater flow and organic loading.

The exhausted granular activated carbon is heated to 1600 to 1800^{0}F to effect volatilization and oxidation of the adsorbed organic contaminants. Oxygen in the furnace is normally controlled at less than 1 percent to effect selective oxidation of contaminants over the carbon itself. A 5 percent loss of activated carbon is an acceptable bench mark upon which granular carbon system economics may be based. Moreover, in the case in which benzidine is removed from wastewater, the reactivation equipment must include an afterburner and an air scrubber to eliminate the possibility of discharging benzidine to the atmosphere.

Granular carbon is transported between the adsorbers and the reactivation equipment by water slurry. Various pumping designs can be employed including centrifugal and diaphram pumps as well as movement using either hydraulic or pneumatic pressure. The transport system is generally enclosed and normally includes flush ports and wide radius bends. Approximately one to three pounds of carbon can be transported per gallon of water used, depending on distance and elevation considerations.

Process Costs

As was indicated above, process costs for the removal of benzidine from wastewaters by adsorption using granular activated carbon cannot be directly established because no continuous-flow, pilot-scale studies have been conducted. Nonetheless, process costs can indirectly be approximated based on previous experience with actual, full-scale industrial installations. Tables III-2 and III-3 summarize data from industrial granular activated carbon systems which are purifying wastewaters that contain toxic or biologically refractive materials. Table III-2 was prepared for those installations which include on-site thermal reactivation, while Table III-3 summarizes data from installations where the carbon is transported to central reactivation facilities. Both tables were compiled by Hager and Rizzo (III-10).

The waste volumes treated annually have been shown for each installation in Tables III-2 and III-3. These vary considerably because of the point of application at each plant. In certain cases, the total plant effluent is treated -- in others, only specific waste streams are treated by adsorption. The latter point of application normally is beneficial from a total cost viewpoint as the quantity of contaminated water is usually less (smaller treatment system required) and the contaminant concentrations are usually higher (greater utilization of the carbon prior to reactivation).

Comparision of Table III-2 and III-3 shows similar costs per 1000 gallons regardless of whether the carbon is reactivated on-site or is reactivated off-

TABLE III-2

TOXIC OR REFRACTORY INDUSTRIAL WASTEWATER TREATMENT GRANULAR CARBON INSTALLATIONS (ON-SITE REACTIVATION)

(Partial Listing)

PLANT	FLOW MILLION GAL/YEAR	TOXIC OR REFRACTORY CONTAMINANTS		TYPE OF THERMAL ON-SITE REACTIVATION	CAPITAL COSTS* ($000)	DIRECT OPERATING COSTS 1000 GALLONS**
		AVERAGE INFLUENT	EFFLUENT OBJECTIVE			
A[19]	6	10,000 mg/l TOC	400 mg/l TOC	Multiple Hearth	350	$20
B[20]	180	370 mg/l phenolics	10 mg/l phenolics	Multiple Hearth	1,300	2
C	70	300 mg/l phenolics	1 mg/l phenolics	Kiln	450	1
D[21]	50	100 mg/l phenolics	1 mg/l phenolics	Multiple Hearth	300	4
E	550	Color	Color removal	Kiln	---	---
F	1100	Color	Color removal	Multiple Hearth	---	---

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* = Includes engineering, construction, adsorption system and reactivation equipment

** = Direct operating costs and do not include depreciation or cost of capital invested.

TABLE III-3

TOXIC OR REFRACTORY INDUSTRIAL WASTEWATER TREATMENT GRANULAR CARBON INSTALLATIONS (CENTRAL REACTIVATION)

PLANT	FLOW	TOXIC OR REFRACTORY CONTAMINANTS			TOTAL ANNUAL COSTS $/000 GALLONS		
	MILLION GALLONS PER YEAR	AVERAGE INFLUENT		EFFLUENT OBJECTIVE	ADSORPTION TREATMENT**	CARBON REACTIVATION***	TOTAL
A*	128	Phenolics TOC	10 mg/l 250 mg/l	0.1 mg/l	0.85	0.80	1.65
B*	18	Phenolics TOC	40 mg/l 300 mg/l	0.1 mg/l	4.00	2.10	6.10
C*	183	Phenolics TOC	100 mg/l 600 mg/l	0.1 mg/l	0.35	0.80	1.15
D	11	TOC	900#/Day	60#/Day	3.50	3.45	6.95
E*	26	TOC	275 mg/l	Specific Toxicity Tests	4.35	2.45	6.80
F*	84	Color TOC	800 mg/l	Color Removal	1.50	0.25	1.75
G	55	Phenolics TOC	1700 mg/l 3000 mg/l	0.1 mg/l	1.00	2.00	3.00
H	55	TOC	1000 mg/l	Specific Toxicity Tests	2.00	9.00	11.00

---

* = Filtration Treatment also

** = Includes: Capital, Maintenance, Insurance & Utilities

*** = Includes: Reactivation Capital, Transportation, Reactivation Utilities & Make-Up Carbon site on a service basis. While the total annual costs appear to be similar, appreciably less initial investment of capital is required at each treatment site if the reactivation system can be obviated by a reactivation service.

Total annual costs shown in Table III-2 are seen to range from $1 to $20 per 1000 gallons. For removing benzidine from the wastewaters of direct dye manufactures it is expected that the cost of activated carbon treatment would likely fall in the range of $10 to $20 per 1000 gallons of wastewater treated.

Concerns of the Benzidine Task Force of SOCMA

The Benzidine Task Force of SOCMA has made known (III-11) several concerns relative to the use of granular activated carbon for the removal of benzidine from wastewater. Those concerns led to their decision to recommend that this technique not be employed. One concern relates to an assumed exposure hazard of carbon which is saturated with benzidine at the 1 to 2 percent level (weight basis). In this regard it is important to recognize that only approximately 0.1 percent of the total surface area of granular activated carbon is at the exterior of the carbon granule. Clearly, 99.9 percent of the total surface area is on the inside of the carbon particle in pores of less than one micron in diameter. Obviously, therefore, the majority of the available surface area for adsorption could not possibly come into direct contact with humans.

If one were to assume that a batch of granular activated carbon were saturated with benzidine at the 1 to 2% by weight level, then less than 0.001 to 0.002% by weight concentration would exist at the exterior surfaces of a carbon granule where the benzidine could potentially come into physical contact with humans. Of course, this is two orders of magnitude less in concentration than the 0.1% level defined by OSHA regulations. Furthermore, it must be remembered that exhausted activated carbon is always transported as a water slurry in pipelines, tanks, etc., and, therefore, never is physically in contact with treatment system operators or other personnel.

The second concern voiced by the Benzidine Task Force related to the potential for discharging benzidine to the atmosphere from a thermal reactivation furnace. Such furnaces are always fitted with an afterburner and an air scrubber to prevent such discharges. These have heretofore been operated on a failsafe basis. Accordingly, one can only conclude that this potential problem can clearly be contained using standard operating procedures and proven technology.

ADSORPTION USING POLYMERIC ADSORBENTS

During recent years considerable bench and pilot-scale research has been directed toward the application of polymeric adsorbents for the removal of color and other refractory organics from industrial wastewaters. Rohm and Haas' Amerlite XAD-4 is an example of such an adsorbent.

To the knowledge of the writer no substantive bench, pilot-scale, or prototype evidence has been obtained regarding the use of polymeric adsorbents for the removal of benzidine from wastewaters. Consequently the technical and economic feasibility of employing such adsorbents for decontaminating wastewaters that contain benzidine cannot be established at this time.

Extensive bench-and pilot-scale studies must be conducted before one can make intelligent judgements regarding the feasibility of using polymeric adsorbents. Requisite studies could logically be completed during a one-year study period. If, upon completion of such a study, this technology were found to be technically and economically feasible, it could likely be implemented within one to two years.

BIODEGRADATION USING THE ACTIVATED SLUDGE PROCESS

A thorough search of the biological literature showed that the earliest studies on the biodegradation of benzidine using activated sludge were conducted by Malaney, et.al. (III-12) and Lutin et.al. (III-13) These studies were conducted during the mid-1960's using Warburg respirometers which contained samples of activated sludge obtained from three different wastewater treatment facilities. The studies that were conducted using sludge concentrations of 2500 and 5000 ppm (mixed liquor suspended solids) and benzidine concentrations of 500 ppm uniformly showed that benzidine was inhibitory or toxic to each of the three sludges employed. The researchers concluded, further, that the removal of benzidine by biooxidation in an activated sludge aeration tank would be insignificant and that the sludges showed no appreciable ability to acclimate to the oxidation of benzidine. They allowed, however, that benzidine might be removed either partially or completely by adsorption onto the sludge mass.

Another experimental study (III-14) conducted during the last quarter of 1973 by Ryckman/Edgerley/Tomlinson & Associates, Inc. (RETA) was commissioned by the Hazardous and Toxic Substance Regulation Office of the Environmental Protection Agency. This study also was conducted using Warburg respirometers and two different types of sludges: an aniline acclimated sludge and a municipal wastewater treatment plant sludge. Concentrations of 2500 ppm (MLSS) activated sludge were employed in the respirometer. The sludge samples were spiked with two different concentration levels of benzidine; 1 and 5 ppm.

Results of the RETA studies showed that benzidine appeared to be slightly inhibitory to both the acclimated aniline and non-acclimated municipal sludges based on oxygen utilization measurements. Nonetheless, both of the sludges showed rather large uptakes of the benzidine during the 12-hour studies. For the case in which a concentration of 1 ppm of benzidine was introduced to the respirometer flasks, 78 and 60 percent uptakes were noted for the acclimated and non-acclimated sludges, respectively. When the benzidine concentration was initiated at 5 ppm, uptakes of 64 and 50 percent were observed. The investigators hypothesized that an adsorption mechanism (adsorption on the biological floc) was involved in removing the benzidine. Although this hypothesis was subsequently tested by RETA, no conclusive proof was obtained to either support or reject an adsorption mechanism. It is noteworthy, further, that RETA suggested that while the biological activity appeared to be retarded for benzidine concentrations of 1 and 5 ppm, bio-degradation of benzidine may actually occur at lower concentrations.

Another Warburg respirometer study was conducted by International Hydronics Corporation under contract to Allied Chemical Corporation (III-15). In essence, these studies were identical to those conducted by RETA: they were conducted (1) with two different kinds of sludges (aniline acclimated and conventional municipal); and (2) with 2000 to 2500 mg/l MLSS. These studies showed that the activated sludge which was aniline acclimated metabolized benzidine more rapidly than did the unacclimated sludge. Moreover, results of the study indicated that concentrations of benzidine in excess of 60 ppm were inhibitory to both types of sludges. The results agree well with those of RETA.

Three recent continuous-flow studies were conducted by International Hydronics Corporation under contract to Allied Chemical Corporation and were supplied to the writer by the Benzidine Task Force of SOCMA (III-15, III-16 and III-17). The first study was conducted using a continuous-flow, bench-scale activated sludge treatment system which contained an activated sludge at a concentration of 3000 mg/l (MLSS) or 1500 mg/l (MLVSS). The system was operated at a hydraulic flow rate of 7.2 liters per day, a hydraulic residence time of 8 hours, and a process loading intensity (F/M) of 0.31 mg BOD/mg MLVSS-day. Benzidine was introduced to the primary sewage effluent feed at a concentration of 0.1 mg/l, (100 ppb).

Results of this one-week study showed that the benzidine clearly was not inhibitory to the biomass as BOD reductions averaged better than 92 percent. The benzidine itself, however, passed through the system essentially untouched. Unfortunately, the study was not continued beyond the one-week period to determine whether or not the sludge would acclimate to the benzidine in the feed and ultimately biologically degrade it. An acclimation period of two months is often required to attain steady-state biodegradation conditions.

The second study also was conducted using a continuous-flow two-liter, bench-scale activated sludge system that contained an aniline acclimated activated sludge at a concentration of 1500 mg/l (MLSS). Acclimation was achieved by introducing aniline to the feed of the activated sludge system --- first at 10 ppm for a one-week period and subsequently by increasing the concentration by 10 ppm increments over a four-week period to a final feed concentration of 50 ppm. Thereafter, benzidine was introduced to the feed at a concentration of approximately 45 ppb while the aniline concentration was maintained at the 50 ppm feed level. The system was operated at a hydraulic flow rate of 7.5 to 9 liters per day, a hydraulic residence time of 5 hours, and a process loading intensity (F/M) of approximately 0.25 mg BOD/MG MLSS-day.

During the study removal of organics averaged 66.6 and 87.4 percent for COD and BOD, respectively. BOD residuals in the effluent of the two-liter reactor averaged 12.5 mg/l. Throughout this period concentrations of benzidine in the effluent averaged 1.83 ppb while the influent concentrations averaged 41.9 ppb for a removal efficiency of 96.11 percent. Of the benzidine that was removed from the aqueous medium, 9.29% was removed by adsorption onto the sludge mass, while 90.71% was biologically metabolized or oxidized. It was reported, furthermore, that the system performed well throughout the nine-week period of study and that no sludge bulking was observed.

A third study was conducted exactly as the second except that an unacclimated municipal sludge was employed for system start-up. During the two-week study removal of organics averaged 82.1 and 89.6 percent for COD and BOD, respectively. COD residuals averaged 28.2 ppm and the average effluent levels for BOD were 9.4 ppm. Throughout the period of study the concentration of benzidine in the effluent averaged 2.02 ppb while the influent concentrations averaged 41.7 ppb for a removal efficiency of 95.1 percent. As for the previous study, the quantity of benzidine adsorbed onto the sludge floc was less than 10 percent of the total quantity removed from the aqueous medium.

No acclimatization period was required for this third study. The sludge apparently immediately biologically metabolized or oxidized the benzidine when fed at the 40 ppb level.

To summarize this sub-section on biodegradation, it can be stated with reasonable certainty that benzidine is toxic to non-acclimated sludges at concentrations of 500 mg/l, is slightly inhibitory at concentrations of 1-5 mg/l and is clearly non-toxic at concentrations of 0.1 mg/l. Moreover, recent studies have shown (1) that benzidine is biodegradable at the 0.045 ppm level acclimated and unacclimated biological sludges and (2) that the vast majority of benzidine that is removed (90%) is biologically degraded while only trace quantities (10%) are incorporated in the sludge mass.

One can conclude, therefore, that benzidine manufacturing wastewaters that have been treated using the nitrous acid oxidation procedure could be discharged directly into an activated sludge wastewater treatment system and that the majority (ca. 90%) of the benzidine that is introduced would be removed by bio-oxidation. A comprehensive research program, however, would be required to establish the proper set of process operating parameters that would yield optimal performance of the biological system. It can be further concluded that benzidine would not adversely affect municipal biological wastewater treatment systems. One would expect that the majority (ca. 90%) of benzidine introduced to a publicly -owned system would be biologically degraded and that less than detectable quantities (1 ppb) would be incorporated in the waste sludge.

Moreover, it can be concluded that wastewaters derived from the manufacture of benzidine-based dyes could be discharged directly to a bio-oxidation treatment system. Since the concentration of benzidine in the dye mother liquor is usually less than 10 ppb. The majority of benzidine as introduced would be removed by biological degradation. However, the application of biological treatment may require PH adjustment and possibly nutrient addition if sufficient other wastes were not available within a plant to mix with the dye production mother liquor.

OTHER POTENTIAL TREATMENT METHODS

Both Case and Ketchen (III-18) and Mytelka and Manganelli (III-19, III-20) reasoned that, in the presence of oxygen, irradiation of large organic molecules in aqueous solution can result in the oxidation and fragmentation of the molecules. Case and Ketchen (III-18) demonstrated that gamma radiation was effective for the removal of color and the carbonaceous content of many dyes and other organic components in textile mill effluents, but that a large variation existed in the radiation dose required. Similarly, Mytelka and Manganelli (III-19, III-20) concluded that when an aqueous solution of the dye Direct Red 79 was subjected to cobalt-60 ionizing radiation, the chemical oxygen demand, total organic carbon concentration, dye concentration, and color of the suspension decreased and that the waste became more amenable to biological oxidation. It is noteworthy, however, that neither of these two studies were conducted using either benzidine or benzidine-based dyes and that no direct evidence that supports the technical feasibility of employing gamma irradiation for the degradation of benzidine currently exists.

Although it is believed that hydrogen peroxide could directly oxidize the benzidine molecule, to the knowledge of the author, no studies have been conducted that demonstrate the technical feasibility of the proposed procedure. This method as well as the gamma irradiation method should be explored to evaluate the technical feasibility of applying these techniques for the complete destruction of benzidine in aqueous solution. If either of these were shown, through experimental study, to be feasible alternatives for the oxidation of benzidine in wastewaters, it would need to be thoroughly investigated and developed prior to actual application. In the case of hydrogen peroxide it is believed that a study period of 3 to 5 years would be required to develop this technology to the point of engineering reality. This R&D period would likely extend to 5 to 7 years in the case of ionizing radiation.

NO AQUEOUS DISCHARGE

The direct dye manufacturing industry has not yet achieved a "no aqueous discharge" management status. If the wastewaters were treated using the granular activated carbon adsorption procedure, however, they likely could be reclaimed and recycled directly to the processing operation to achieve a no discharge condition. Conversely, if the nitrous acid procedure were employed for oxidation of the benzidine in the wastewater, then a no discharge condition could probably only be achieved only through multiple-effect evaporation and subsequent disposal of the resultant solids. Costs for such a reclamation system would probably approach $100 per 1000 gallons of wastewater treated (25 cents per pound of benzidine produced). Alternatively, multiple-effect evaporation could potentially, by itself, provide a no discharge management status.

SUMMARY

Of the potential treatment technologies that are available for the removal of benzidine from process wastewaters, only the nitrous acid oxidation method has been implemented at the plant scale (Allied Chemical Corporation and GAF Corporation) and shown to be effective for the concentrated benzidine manufacturing wastes. It is to be noted that this process was employed only for the treatment of benzidine manufacturing wastewaters. Residual levels of benzidine in the nitrous acid treated effluent usually were found to be less than 10 ppb.

Benzidine-based dye manufacturing wastewaters can be treated relatively inexpensively by the bio-degradation process. Due to biological toxicity, however, this process probably cannot be employed for the direct treatment of benzidine manufacture wastewaters prior to a pretreatment step such as the nitrous acid oxidation process.

Allied Chemical Corporation, Fabricolor, Inc. and GAF Corporation discharge their wastewaters to municipal biological wastewater treatment systems. The final product wastewaters, after biological treatment, should show no detectable benzidine.

No other benzidine treatment technologies have been implemented at the plant-scale; in fact, none have been evaluated beyond the bench-scale. Consequently, plant-scale process efficiencies and costs have not been established for any of the processes considered other than the nitrous acid oxidation process. A tabular comparison of the potential treatment methods has been given in Table III-4.

The fact that the ranges for actual or projected process costs given in Table III-4 are broad is due to the fact that benzidine production methods vary considerably with respect to the quantity of process wastewaters generated. If the wastewater volumes produced are high, then the associated costs are also respectively higher.

TABLE III-4

COMPARISON OF POTENTIAL TREATMENT METHODS

Type of Treatment	Level of Development and/or Application	Effectiveness	Cost ¢/# product
A. Benzidine Manufacturing Wastewaters			
Oxidation with Nitrous Acid (Pretreatment Only)	Full Scale	10 ppb	2-12 (actual)
Oxidation with Ozone	Bench-Scale (Preliminary Only)	1-10 ppb (proj.)	100-500 (proj.)
Adsorption onto Activated Carbon	Bench-Scale (Preliminary Only)	1-10 ppb (proj.	1-10 (proj.)
Adsorption onto Polymeric Adsorbent	None	1-10 ppb (proj.)	Unknown
No Discharge/Evaporation	None	N/A 2/	25 (proj.)
B. Benzidine-based dye Manufacturing Wastewaters			
Biodegradation (Secondary Treatment Only)	Bench-Scale	toxic for inf. conc. = 10 ppm 1-10 ppb for inf. conc.=1 ppm	0.02 per poundage (proj.) 1/

1/ Footnote: For treatment of dye mother liquors; (basis 0.40/thousand gal.)
2/ Includes pretreated benzidine manufacturing wastes

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SECTION IV

DISCHARGE OF BENZIDINE TO PUBLICLY OWNED TREATMENT WORKS

DISCHARGE LOCATIONS

Each of the three benzidine-based dye manufacturers discharges its wastewaters to a regional sewer authority. Allied Chemical Corporation discharges its wastewaters after pretreatment to the Buffalo Sewer Authority which operates a primary treatment works on Bird Island. By 1977 this is to be expanded to a secondary activated sludge system which will discharge to the Niagara River.

GAF Corporation discharges its wastewaters to the Rensselaer County Sewer District No. 1. The district is currently in the process of placing on-line a conventional activated sludge system which has provisions for chlorination and sludge treatment by the Zimpro wet oxidation process. Construction was to have been completed by 17 November 1975 and the system was to have been entirely operational by 2 January 1976. GAF has also constructed pretreatment facilities in association with Winthrop Laboratories. The discharge of Rensselaer Sewer District plant is to the Hudson River.

Process and sanitary effluents of Fabricolor, Inc. are combined and flow into a sewer system (Passaic Valley Sewer Authority) which parallels but does not enter the Passaic River in the vicinity of Paterson, New Jersey. The municipal system combines with other municipality discharges along a sewer line route to the north shore of Newark-Bay where all the wastewater receives primary treatment and then is piped across the bay to an outfall below water level in the Hudson River in the lower portion of Upper New York Bay.

PRETREATMENT SYSTEMS

Allied Chemical Corporation .... As indicated above, all process wastewaters from Allied's Buffalo Dye Plant are collected and combined in a process waste sewer system. This, of course, includes the discharge of the nitrous acid treatment system. The sewer discharges into a pretreatment system which consists of equilization, neutralization and clarification of the aqueous stream. A schematic flow diagram is shown in Figure IV-1. A brief description of each of the unit processes follows:

> Collection -- Process wastes are collected from the various manufacturing areas and discharged to the pretreatment plant via three wet wells equipped with three pumps. Screens are provided to protect the pumps from debris. In normal operation, one pump operates continuously. The other pumps serve as standbys providing reserve capacity for peak flows. These are activated by high level switches in the wet wells. The pumps raise the wastewater from the wet wells through a Parshall flume to equilization basins.
>
> Equilization -- Two earthen-dike lagoons, lined with clay, operate in parallel to receive the process effluent and provide capacity to equilize variations in flow and concentration of pollutants. Each lagoon has a nominal capacity of one million gallons and is provided with a perforated air header throughout its entire length. Low pressure air (10 psig) is introduced into these headers to provide gentle mixing of the lagoon's contents to prevent sedimentation of suspended solids.
>
> Neutralization -- Neutralization of the process wastewaters is achieved by adding a lime slurry (10 - 12% $Ca(OH)_2$) to either or both of two agitated reactors of 10,000 gallon capacity. The pH of the effluent has a variation of 8.0± 0.5.
>
> Clarification -- Neutralized waste process water flows to the reaction well of a solids-contact clarifier by gravity where it is contacted with previously precipitated solids. A polyelectroyte flocculant is added to aid in floc formation. The clarifier has a hydraulic residence time of two to six hours depending on flow rates. Clarifier overflows are subsequently discharged to the City of Buffalo Sewer Authority.
>
> Thickening -- Sludge settled in the clarifier (1 - 2% solids) is continuously pumped to a conventional thickener where the solids content is increased to 3 to 5%. The overflow from the thickener is returned to the neutralization reactors. The solids residence time in the thickener varies according to flow and sludge production rates. Generally the residence time varies between one to two weeks.

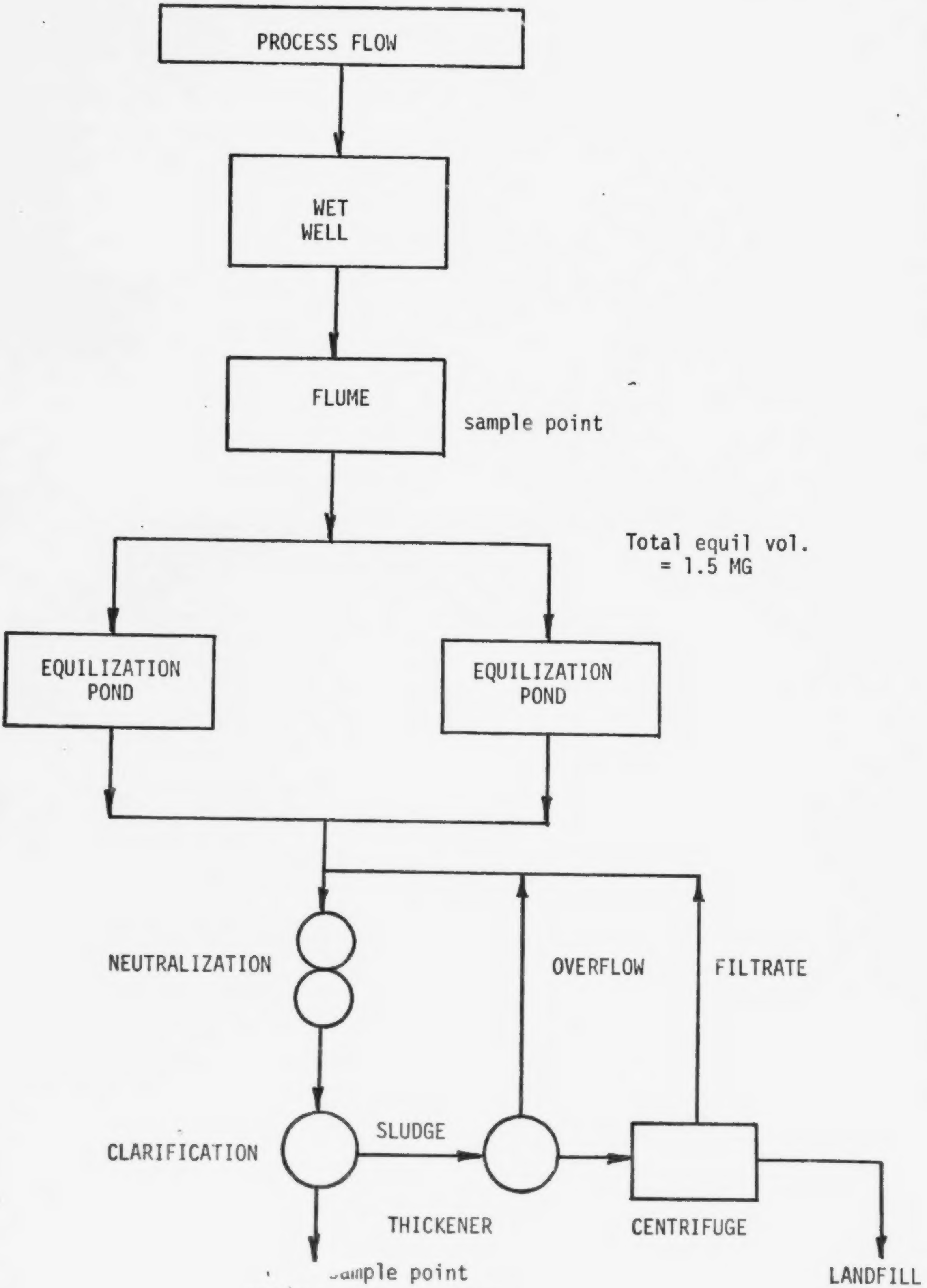


FIGURE IV-1

BUFFALO DYE PLANT PRETREATMENT FACILITY

> Dewatering -- Thickened sludge is pumped to one of two centrifuges where final dewatering is accomplished (20% solids). Polyelectrolytes are added in this operation to improve process efficiency. Dewatered sludge is collected and disposed of in sanitary landfill sites approved by State and County Agencies. The centrate is returned to the neutralization reactors.

Analyses for benzidine were performed on the clarifier over-flow prior to discharge to the Buffalo Sewer Authority during the period which extends from 20 March to 3 June 1974. These have been tabulated in Table IV-1. All analyses were performed on 24-hour composite samples collected at 0800 hours. In addition to a leak in the Vallez filter which occurred on 31 March 1974 and was noted earlier, an incompletely reacted dye batch of "Big Black" containing benzidine was sewered in Building 125. This was reflected in high loadings on 11 and 13 May.

The data shown in Table IV-1, as before, was analyzed statistically in two ways: -- including (Mode 1) each of the 75 data points assuming that the 18 samples that showed less than the detectable concentration had concentration of 5 ppb; those values which fell outside the 99% confidence limit. The analysis showed the following for loadings per day:

	Mode 1	Mode 2
Average	0.51	0.38
Std. Deviation	0.76	0.27
High 95% Conf.	2.0	0.9
High 99% Conf.	2.5	1.2

One can conclude, therefore, that benzidine loadings to the Buffalo Sewer Authority of less than 0.41 pounds per day can be achieved at the 99 percent confidence level if leaks and batch discharges are either eliminated or accounted for through suitable treatment provisions. Average daily loadings of 0.33 pounds should be achievable when the nitrous acid treatment method is employed for benzidine manufacture wastes and the total wastewater stream is pretreated

TABLE IV-1

Benzidine in Pretreated Wastewaters of the Buffalo Dye Plant

Date	WW/Flow (10^6 lbs/day)	Benzidine Conc. (ppb)	Benzidine Loading (lbs/day)
3-20-74	12.0	40	0.5
3-21-74	13.2	30	0.4
3-22-74	13.9	20	0.2
3-23-74	12.9	30	0.4
3-24-74	10.4	40	0.4
3-25-74	11.9	*	-
3-26-74	13.4	10	0.1
3-27-74	12.5	70	0.9
3-28-74	12.9	60	0.7
3-29-74	11.4	50	0.6
3-30-74	10.7	30	0.3
3-31-74	8.7	30	0.3
4-1-74	11.5	140	1.1
4-2-74	14.3	120	1.5
4-3-74	11.9	-	-
4-4-74	12.9	40	0.5
4-5-74	10.9	80	0.9
4-6-74	9.2	40	0.4
4-7-74	7.2	120	0.9
4-8-74	11.7	40	0.5
4-9-74	12.7	50	0.7
4-10-74	14.3	30	0.4
4-11-74	15.4	50	0.8
4-12-74	15.3	*	-
4-13-74	10.1	40	0.4
4-14-74	9.0	40	0.4
4-15-74	9.6	*	-
4-16-74	12.7	*	-
4-17-74	12.9	*	-
4-18-74	13.1	*	-
4-19-74	13.1	*	-
4-20-74	12.8	*	-
4-21-74	10.8	10	0.1
4-22-74	8.3	20	0.2
4-23-74	12.5	60	0.7
4-24-74	12.4	30	0.4
4-25-74	13.0	60	0.8
4-26-74	12.3	*	-
4-27-74	11.4	*	-
4-28-74	9.0	*	-
4-29-74	13.1	*	-
4-30-74	7.2	40	0.3
5-1-74	10.6	60	0.7

Note: * indicates a concentration $<$2 - 5 ppb

TABLE IV-1 (cont.)

Date	WW/Flow (10^6 lbs/day)	Benzidine Conc. (ppb)	Benzidine Loading (lbs/day)
5-2-74	12.8	40	0.5
5-3-74	11.2	20	0.2
5-4-74	10.4	20	0.2
5-5-74	7.5	50	0.4
5-6-74	8.6	100	0.8
5-7-74	10.1	70	0.7
5-8-74	11.8	*	-
5-9-74	13.7	*	-
5-10-74	13.9	40	0.6
5-11-74	13.6	150	2.0
5-12-74	6.1	140	0.9
5-13-74	6.9	610	4.2
5-14-74	13.4	170	2.2
5-15-74	13.6	50	0.7
5-16-74	13.5	*	-
5-17-74	14.5	20	0.3
5-18-74	15.5	310	4.7
5-19-74	8.7	10	0.1
5-20-74	12.4	80	1.0
5-21-74	13.4	20	0.3
5-22-74	13.5	*	-
5-23-74	12.9	40	0.5
5-24-74	12.8	30	0.3
5-25-74	8.9	10	0.1
5-26-74	8.4	20	0.2
5-27-74	8.4	40	0.3
5-28-74	7.7	*	-
5-29-74	11.4	*	-
5-30-74	11.3	30	0.3
5-31-74	11.1	50	0.5
6-1-74	11.8	90	1.1
6-2-74	9.1	80	0.7
6-3-74	10.2	60	0.6

Note: * indicates a concentration < 2 - 5 ppb as described.

Analyses for benzidine were also performed on the centrifuged sludge which is disposed of in sanitary landfill sites approved by the New York State Department of Environmental Conservation and appropriate county agencies. Results of the analyses are presented in Figure IV-2 for the period extending from 20 March through 15 December 1974.

Qualitatively, one can observe that the benzidine content of the sludge varied greatly throughout the period of study. Initially (March through June 1974) the benzidine concentration ranged from 3 to 12 ppm. Since June 1974, the benzidine content of the precipitated neutralization sludge increased dramatically to 700 ppm - subsequently dropping to levels of 50 ppm by December of 1974.

Sludge quantities generated vary widely depending upon the quality of the process waste effluent among other factors. From January 1974 through April 1975 an average of 23.33 tons of dry solids were produced per week although the solids production ranged from zero to 70 tons per week.

Attempts to conduct a mass balance on benzidine for the Pretreatment Works of Allied's Buffalo Dye Plant have been unsuccessful. This is primarily due to the fact that a considerable, but unknown, quantity of solids have accumulated in the equilization lagoons.

Discharges of phenol from the Pretreatment Works to the Buffalo Sewer Authority were monitored during a 14-day period beginning 19 October 1974. Data for this period is presented in Table IV-2. All analyses were performed on 24-hour composite samples using the 4-amino anti-pyrene method. The majority of the phenol loading is attributed to the process wastes from the manufacture of methyl violet (III-3).

FIGURE IV-2 BUFFALO DYE PLANT PRETREATMENT PLANT SLUDGE BENZIDINE CONCENTRATIONS

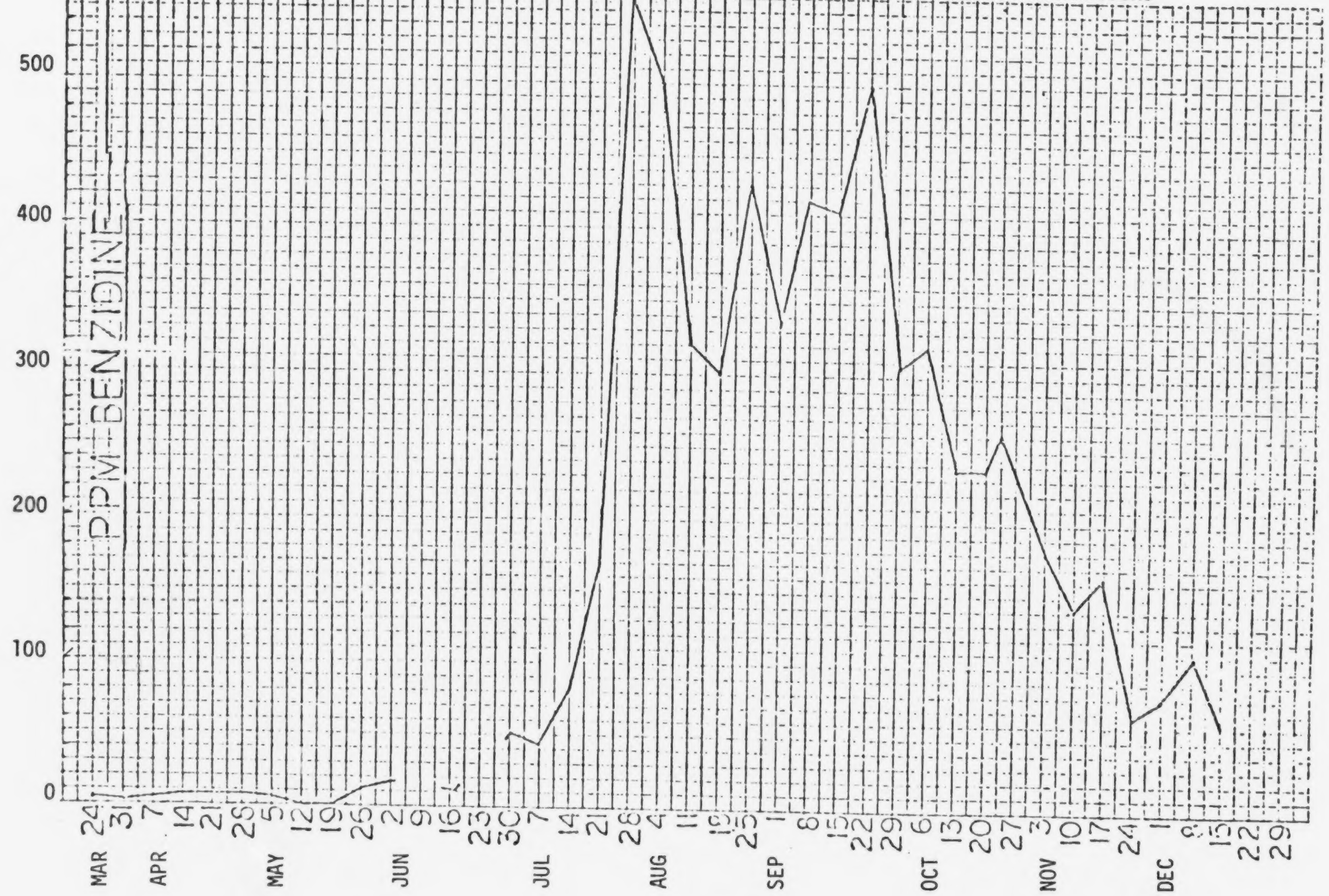


TABLE IV-2

Phenol in Pretreated Wastewaters of the Buffalo Dye Plant

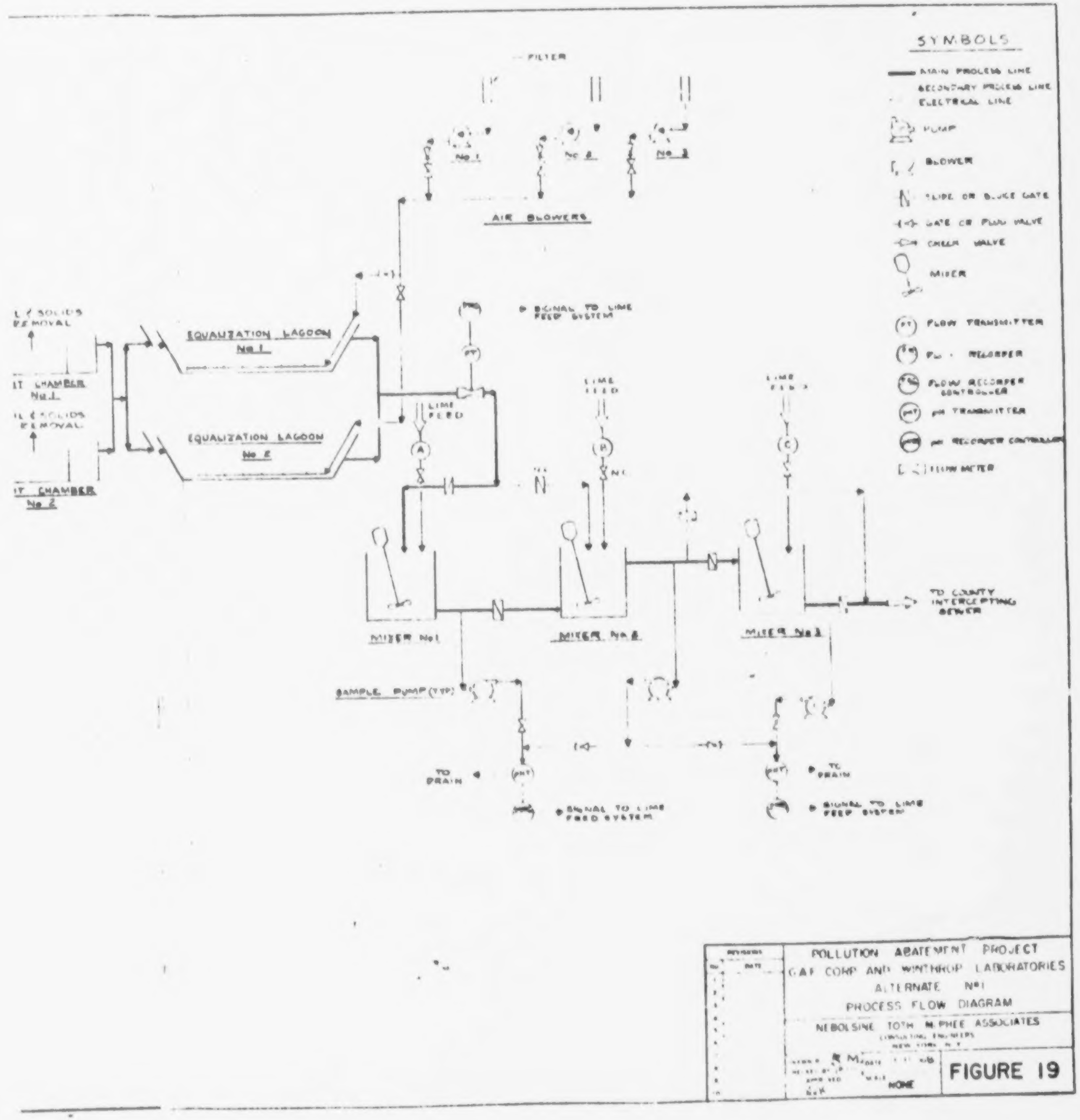
Date	(10^6 lbs/day)	Phenol Conc. (ppm)	Phenol Loading (lbs/day)
10-19-74	12.4	1.61	20
10-20-74	12.3	1.49	18
10-21-74	13.4	0.56	8
10-22-74	13.0	2.83	37
10-23-74	14.1	1.01	14
10-24-74	14.6	0.63	9
10-25-74	14.5	1.88	27
10-26-74	14.0	1.23	17
10-27-74	11.9	0.49	6
10-28-74	13.0	0.17	2
10-29-74	12.0	2.30	28
10-30-74	13.7	2.98	41
10-31-74	14.7	3.95	58
11-1-74	14.8	2.24	33

GAF Corporation .... As noted previously, GAF Corporation is currently nearing the completion of a pretreatment facility. The facility is to be jointly owned and operated by GAF and Winthrop Laboratories, a subsidiary of Sterling Drug Company. A schematic flow diagram for this system which was placed on-line in January 1976 is shown in Figure IV-3. A brief description of each of the unit processes as provided by the design engineer follows:

> Collection and Pumping -- The pumping station will be located at the junction of the GAF and Winthrop outfall sewers. From that point the waste flows are pumped up to the equilization basins. The pumping arrangement for the combined GAF and Winthrop flow will consist of four dry pit-type, horizontal centrifugal pumps, each with a maximum capacity of 1800 gpm. Preceding the pumping station, a metering chamber will be provided to seperately meter and sample the GAF and Winthrop discharges. The flow data will be transmitted to indicating, recording, and totalizing meters located in the pumping station. Composite samples of the wastes will be analyzed for pH, BOD and suspended solids. This data will be used to proportion charges at both the pretreatment and secondary treatment plants.
>
> Grit Chambers -- To prevent grit from depositing in the equilization basins, two grit chambers will be provided. Each chamber tank will be acid-proofed and brick lined. The grit and heavy settleable solids will be cleaned manually by alternately taking each tank out of service.
>
> Equilization Basins -- To ease the problems normally encountered in neutralizing industrial wastes, the raw wastes, after being degritted, will pass through two clay-lined equilization basins. The purpose of the basins is to level out flow variations and rapid changes in pH and other characteristics of the wastes. The wastes will be discharged uniformly from each basin and will be mixed by use of low pressure air jets.
>
> Neutralization -- Following the equilization basin, lime or caustic will be mixed with the wastewater stream in a series of three rapid mixers until the pH of the wastewater has been elevated into the range of 5.5 to 8.5. Three mixing chambers will be provided to introduce the neutralizing agent into the waste stream. Each chamber will have a detention time of five minutes.

OCCURRENCE OF BENZIDINE IN POTW'S

Analyses (IV-1, IV-2) for benzidine in samples collected from the primary sedimentation effluent of the Buffalo Sewer Authority's treatment works on Bird



POLLUTION ABATEMENT PROJECT
GAF CORP AND WINTHROP LABORATORIES
ALTERNATE No 1
PROCESS FLOW DIAGRAM

NEBOLSINE TOTH McPHEE ASSOCIATES
CONSULTING ENGINEERS
NEW YORK, N.Y.

FIGURE 19

Island showed concentrations at the level of detectability (0.2 to 0.5 ppb). It is to be noted that these wastewaters were not subjected to biological oxidation. Through dilution (ca. 100-fold) and possible degradation in the transport system the benzidine concentrations were diminished to the level of detectability.

EFFECTS OF BENZIDINE ON PUBLICLY OWNED TREATMENT WORKS

Based on the results of the biodegradation studies cited in the previous section (III), it is clear that any municipal biological (activated sludge or trickling filter) wastewater treatment system would not encounter operational difficulties of benzidine were present in the influent at concentrations less than 1 ppm. The biological studies showed, furthermore, that when benzidine is introduced to an activated sludge system at the 50 ppb level, approximately 95 percent of the benzidine is biologically degraded.

When the nitrous acid oxidation procedure is employed for the decontamination of benzidine manufacture wastewaters, the concentration of benzidine in the combined wastewaters of the manufacturing facility is generally less than 50 ppb. It is readily apparent, therefore, that any benzidine introduced to publicly owned treatment works would be biodegraded even if the benzidine wastewaters would be directly introduced to the biological treatment reactor without dilution. Accordingly, one can conclude that benzidine in the wastewaters of publicly owned treatment works would be degraded and would have no effect on the operation of such works. Residual concentration of benzidine in the effluent of such treatment works should always be less than the level of detectability (0.2 ppb).

Because municipal biological sludges are usually anaerobically digested (a biological process), it is important also to consider the potential adverse effects that benzidine would have on this process since small quantities of benzidine adsorb on the aerobic sludge mass. Unfortunately, no process performance information is available in this regard. Nonetheless, because less than 10 percent of the benzidine introduced to an activated sludge system (50 ppb level) is actually incorporated in the sludge and because such low levels of benzidine have no effect on aerobic biological activity, one can opine with reasonable certainty that the occurrence of benzidine in municipal wastewaters would not affect the operational performance of anaerobic digesters.

In the case of benzidine and benzidine-based dye manufacturers, one should also consider the effects of the possible incorporation of benzidine-bases dyes into an activated sludge mass which ultimately is anaerobically digested. The reducing environment found in an anaerobic digester may serve to reduce the dyes to the precurser, benzidine. Although no direct evidence is available to support or refute this hypothesis, some indirect evidence has been gathered by Flege (IV-3). His research showed that certain non-benzidine based dyes which are usually used for dyeing synthetic fibers were broken down during anaerobic digestion to form the intermediates that originally were used for synthesizing the dyestuff. Some of these intermediates were identified as being carcinogenic. This latter evidence, however, is very circumstantial and should not, therefore, be construed as being indicative of what would occur in the case of benzidine-based dyes. Even if such reduction of benzidine-based dyes would occur, the concentrations would likely be sufficiently low so as not to be a problem.

EFFLUENT LIMITATIONS FOR INDUSTRIAL DISCHARGES

Allied Chemical Corporation .... Currently, no effluent limitations exist for industrial discharges into sewers operated by the Buffalo Sewer Authority. Such limitations have, however, been proposed. These have been tabulated in Table IV-3. No reference is made to benzidine, benzidine-based dyes, or any other specific organic materials other than phenol.

TABLE IV-3

PROPOSED EFFLUENT LIMITATIONS FOR INDUSTRIAL DISCHARGES INTO SEWERS OPERATED BY THE BUFFALO SEWER AUTHORITY

PARAMETERS	PROPOSED LIMITS
Suspended Solids	Surcharge over 250 mg/l
BOD	Surcharge over 250 mg/l
COD5	No determination
TOC	No determination
Oil & Grease	50 mg/l
Ammonia as N	No limit
Phenol	0.1 mg/l
Mercury	0.1 mg/l
Arsenic	0.1 mg/l
Chlorides	10,000 mg/l
Dissolved Solids	10,000 mg/l
Total Phosphates	Surcharge over 5 mg/l
Cyanide	Complex 0.8 mg/l Free 0.1 mg/l
Sulfates	500 mg/l as Na_2SO_4
pH	5.5 - 9.5
Silver	0.1 mg/l
Aluminum	No decision
Boron	1.0 mg/l
Barium	2.0 mg/l
Calcium	No limit
Cadmium	0.2 mg/l
Chromium	Total 2.0 mg/l Trivalent 1.9 mg/l Hexavalent 0.1 mg/l
Copper	0.4 mg/l
Iron	No limit
Manganese	2.0 mg/l
Nickel	2.0 mg/l
Lead	0.1 mg/l
Antimony	No decision
Tin	No limit
Zinc	0.6 mg/l

GAF Corporation .... Effluent limitations imposed on GAF Corporation require the construction of pretreatment facilities such that the effluent discharged from the facilities shall be "*transportable, treatable and in compliance with the following requirements:*

(1) The effluent shall be equilized and neutralized with lime to a pH range between 5.5 and 8.5.

(2) The effluent may contain a variety of insoluble materials illustrated by the following examples:

aluminum hydroxide
barium sulfate
calcium carbonate
calcium fluoride
calcium molybdate
calcium phosphate
calcium tungstate
chromium hydroxide
charcoal
zinc hydroxide
cobalt hydroxide
copper hydroxide
filter aid
insoluble organics
iron hydroxide
lead hydroxide
manganese hydroxide
waste sludge
nickel hydroxide

(3) The effluent may contain a wide variety of inorganic ions as illustrated by the following examples:

ammonium
bromide
borate
calcium
chloride
fluoride
iodide
magnesium
manganese
molybdate
nitrate
phosphate
nitrite
potassium
sodium
sulfate
sulfide
sulfite
thiosulfate
tungstate

(4) The effluent may contain soluble organic molecules in great variety as illustrated by the following examples:

acetate
acetic acid
aceto nitrite
acetone
benzene
butyric acid
dimethylformamide
formaldehyde
isopropyl alcohol
isopropyl acetate
methyl alcohol
oxalic acid
para-cresol
phenol

Dowtherm A
ether
ethyl alcohol
ethylene dichloride
phihalates
tartaric acid
tetrahydroforam
toluene

(5) The most evident biologically resistant material in the effluent is color. Normally, this will contribute a color of 4000 APHA units to a volume of 4,500,000 gallons."

It is noteworthy that again no reference is made to benzidine or benzidine-based dyes.

Fabricolor, Inc. .... No pretreatment requirements have been imposed on Fabricolor, Inc. by the Passaic Valley Sewer Authority.

LITERATURE CITED

IV-1 Anon. "Survey of the Buffalo Sewer Authority Effluent for the Presence of Benzidine" Great Lakes Laboratory, State University College of Buffalo, 25 July 1975.

IV-2 Czarnecki, A. J. "Buffalo Dye Plant Benzidine Study: Benzidine Loadings at the BSA Outfall to the Niagara River" Internal Memorandum of the Buffalo Dye Plant, August 1975.

IV-3 Flege, R. K., "Determination, Evaluation and Abatement of Color in Textile Plant Effluents." Completion Report, OWRR Project #B-012-GA, Georgia Institute of Technology, Atlanta, GA (1968).

SECTION V

FEASIBLE TECHNOLOGIES FOR BENZIDINE TREATMENT

The nitrous acid oxidation treatment procedure as described in Section III of this report and applied by GAF Corporation and Allied Chemical Corporation is the only treatment technology that, at this time, can be considered to be feasible as a treatment method for benzidine. The following justifications are given:

(1) None of the other treatment processes considered in Section III can be judged feasible at this time because they have not been tested or evaluated beyond the bench-scale in the laboratory. Circumstantial field evidence would indicate, however, that the biodegradation process is feasible for treating benzidine wastewaters containing less than 1 ppm benzidine.

(2) Although biodegradation was shown to be effective, it can be employed only as a secondary treatment process for benzidine manufacturing wastewater because acceptable process efficiencies can be obtained only for influent benzidine concentrations less than 1 ppm. For benzidine-based dye manufacturing wastewaters, however, the biodegradation process can be employed as a primary treatment method.

(3) The nitrous acid treatment technology can be employed as a pretreatment method which preceeds a biodegradation system.

(4) Treatment efficiencies obtained through nitrous acid oxidation at the Allied's Buffalo Dye Plant are such that the concentration of benzidine in the combined wastewaters prior to neutralization averaged 47 ppb while the mass discharged was 0.38 pounds per day. After neutralization and prior to discharge to the Buffalo Sewer Authority collection sewer, the concentration averaged 35 ppb and the mass discharged was 0.33 pounds of benzidine sulfate per day.

(5) In the case of Allied Chemical Corporation as well as at GAF and Fabricolor, Inc. (the only existing producers of benzidine), the pretreated wastewaters are discharged to municipal sewers. At the Buffalo wastewater treatment plant no benzidine (<1 ppb) can be detected in the wastwater matrix (refer to Section IV). Moreover, at such dilute levels benzidine would have no effect whatsoever on the operation of publicly owned treatment works (refer to Section IV).

(6) Pretreatment of benzidine manufacture wastewaters which would be discharged by new sources to publicly owned treatment works could also be achieved by the nitrous acid oxidation procedure. Treatment efficiencies would likely equal or exceed those obtained at Allied's Buffalo Dye Plant.

(7) If a new benzidine manufacturing facility were installed at a location where the wastewater would be discharged directly to a receiving watercourse, the nitrous acid oxidation procedure would also be suitable for the treatment of benzidine production wastewaters. Assuming treatment efficiencies equal to those obtained by Allied Chemical Corporation, benzidine concentrations in the wastewater discharge would likely be less than 25 ppb.

In the event that the effluent standards for benzidine were to be set at a level lower than the 10 to 50 ppb range, then additional treatment would be required as an add-on for new facilities discharging directly to a watercourse. As demonstrated in Section III, such additional treatment could be achieved biologically. Discharge concentrations of benzidine after oxidation with nitrous acid and subsequent biodegradation would be expected to be in the 1 to 5 ppb range.

(8) The nitrous acid treatment technology can be readily implemented within one year of the date of promulgation of standards.

(9) Costs associated with treating wastewaters containing bencidine ranged from 2 to 12 cents per pound of product. The cost varied due to different production methodologies.

Although only the nitrous acid treatment process has been installed heretofore and is feasible at this time, the adsorption technologies (activated carbon and polymeric adsorbents) should further be explored and researched to evaluate their potential for application to new direct dischargers.

SECTION VI

CONTROL OF WASTEWATER DISCHARGES OF BENZIDINE-BASED DYE APPLICATORS

Benzidine-based dyes are used principally in three industrial areas: paper, leather, and textiles. According to the latest Tariff Commission Data available, the market for benzidine dyes in 1973 was approximately 30 million pounds. Of this total market approximately 40 percent of the total volume is consumed in the manufacture of paper, 25 percent by the textile industry, 15 percent for leather production, and the remaining 20 percent in various other industries. The dyestuff comprises approximately 1, 2-3, and 4-6 percent of the finished weight of paper, textile goods, and leather products, respectively, for which it is used.

Because approximately 2 to 20 ppm of benzidine is contained in the direct dyes as they are used by the dye applicators, the possibility exists that the dye applicators themselves could potentially cause pollution simply by discharging the benzidine that entered their processing system as an impurity. In this regard the Benzidine Task Force of the Synthetic Organic Chemicals Manufacturing Association has recommended the use of a mass balance monitoring analysis in lieu of a chemical analysis to ascertain that dye applicators meet EPA guidelines. It is noteworthy that the mass or materials balance approach is routinely employed by the chemical engineering profession.

The "mass balance" monitoring approach requires the use only of inventory records: i.e., knowing how many pounds of benzidine-based dyes were used during a particular time period and knowing the total quantity of water discharged from the plant during the same time period, one can calculate the maximum concentration of benzidine that could possibly be present in the wastewater assuming that 20 ppm of benzidine is present in the dye and that all of it is discharged into the wastewater. The "mass balance" or inventory monitoring approach is more economical than an analytical monitoring approach which would require routine sampling and analysis and the acquisition of relatively sophisticated analytical instrumentation.

To evaluate the efficacy of using the mass balance approach as proposed by SOCMA, three types of scoping surveys were conducted. The first consisted of site visits to three industrial firms that represented the paper, textile, and leather industries. The second involved a questionaire that was forwarded to five manufacturers of paper, leather and textile goods. The final survey consisted of an analytical survey of benzidine contained in the wastewaters of industries in the three industrial categories.

ANALYSIS OF MASS BALANCE APPROACH

Site Visit Surveys

Textile: Clyde Fabrics, Inc.... Clyde Fabrics, Inc. of Newton, North Carolina manufacturers and dyes fabric for the construction of work gloves. Benzidine-based dyes comprise approximately 80 percent of its entire dye usage. Consequently, a survey of benzidine levels which occur in the wastewater discharges of this particular industry could truly be classified as a "heavy use" situation.

If one were to assume that the concentration of benzidine in the benzidine-based dyes used by Clyde Fabrics, Inc. is 20 ppm as the maximum level certified by the dye manufacturer, then one can calculate the maximum concentration of benzidine that could be present in the wastewater by the mass balance analysis. Such calculations were conducted for data obtained for the month of June 1975. The calculations which have been tabulated in Table VI-1 show calculated maximum possible benzidine concentrations in the exhausted dye liquors ranging from 6.63 to 17.66 ppb with an average of 13.32 ppb and a median value of 13.07 ppb. The average calculated total mass discharge of benzidine is 0.0101 pounds per day.

TABLE VI-1

CALCULATED MAXIMUM POSSIBLE BENZIDINE CONCENTRATIONS IN THE WASTEWATERS OF CLYDE FABRICS, INC.

Date	Dye Usage (pounds)	Water Usage (1000's gallons)	Benzidine Conc. (ppb)
6-2-75	602.2	99	14.59
6-3-75	424.15	84	12.11
6-4-75	545.15	100	13.07
6-5-75	418.7	80	12.55
6-6-75	586.5	93	15.12
6-7-75	259.7	44	14.15
6-9-75	444.83	109	9.79
6-10-75	427.06	81	12.64
6-11-75	706.43	102	16.61
6-12-75	516.78	86	14.41
6-13-75	368.3	50	17.66
6-16-75	619.55	111	13.38
6-17-75	548.65	104	12.65
6-18-75	574.95	117	11.78
6-19-75	731.3	103	17.03
6-20-75	431.8	69	15.01
6-23-75	828.45	128	15.52
6-24-75	512.06	115	10.68
6-25-75	588.96	113	12.50
6-26-75	320.7	116	6.63
6-27-75	202.9	41	11.87
Average	507.58	92,619	13.32

Even though a mass balance calculation should be conducted assuming that all of the benzidine in benzidine-based dyes is discharged with the exhausted dye liquors, one must recognize that some of the benzidine is actually transferred to the product. Such transfer of benzidine to the product has been estimated at 25 to 50 percent of the total benzidine present (VI-1). To evaluate this estimate of benzidine transfer, exhausted dye liquor of Clyde Fabrics, Inc. were analyzed during July 1975. The results obtained have been tabulated in Table VI-2. Based on these results (which are not directly comparable with the data of Table VI-1 due to different period of analysis) one can estimate that approximately 75 percent of the benzidine was transferred to the cloth.

Assuming that the benzidine which is discharged by Clyde Fabrics, Inc. to the City of Newton, North Carolina wastewater collection system is conservative (i.e., not degraded), the concentration of benzidine in the influent to the Newton wastewater treatment plant is calculated to be either 0.822 or 0.216 ppb depending on whether the concentration of benzidine in the discharge of Clyde Fabrics, Inc. averages 13.32 or 3.5 ppb, respectively.

At Newton, North Carolina the wastewater treatment system consists of (1) screening and grit removal, (2) primary clarification, (3) biological trickling filtration, (4) secondary clarification, and (5) chlorination. Samples of wastewater collected at the influent to the chlorine contact chamber and analyzed for benzidine (VI-2) showed concentrations less than the level of detectability (0.2 ppb).

Leather: S. B. Foot Tanning Company .... S. B. Foot Tanning Company of Red Wing, Minnesota processes and dyes beef hides for ultimate sale to the shoe manufacturing industry. The company is a medium sized tanner, tanning approximately 6500 to 6800 sides per day.

The calculated mass balance benzidine concentration that could be present in the dye house blow-down wastewaters is 0.38 ppb (basis: 20 ppm benzidine

TABLE VI -2

BENZIDINE CONCENTRATIONS IN EXHAUSTED DYE LIQUORS AT CLYDE FABRICS, INC.

Date	Sample Source	Benzidine Conc. (ppb)
7-17-75	Machine #1	3.1
7-17-75	Machine #2	4.2
7-17-75	Machine #3	2.2
7-22-75	Machine #2	4.5
Average		3.5

in dye). Upon dilution with other process wastewaters the concentration is reduced to 0.25 ppb. The average calculated total mass discharge of benzidine is 0.0144 pounds per day.

S. B. Foot Tanning Company operates its own wastewater treatment plant which consists of two primary clarifiers, a four million gallon aerated lagoon, two secondary clarifiers, and a chlorine contact chamber. The treatment system has a 4.4 day hydraulic detention time at the current 6.9 MGD wastewater flow rate. An EPA demonstration grant was awarded to S. B. Foot Tanning Co. to demonstrate the performance of their treatment system as BPCTCA. The project terminated late in 1974. The final report is currently in review and is, therefore, not yet available.

Although the concentration of benzidine in the wastewater is at the level of detectability, one major potential problem must be addressed at the S. B. Foot Tanning Company. That is, in the tanning operation the possible reduction of benzidine-based dyes to the parent material, benzidine, exists. This is due to the fact that large quantities of sulfides (2000 lbs. NaHS and 1000 lbs. Na_2S) are used per day in the dehairing operation. Even though 35 percent of the sulfides are recovered for recycle, the concentration of sulfides in the influent to the wastewater treatment facility is approximately 200 ppm. Since the wastewaters are not segregated, a rather high potential exists for the reduction of benzidine-based dyes.

To evaluate the potential magnitude of this problem a "likely" situation can be calculated. The production manager of S. B. Foot Tanning Company estimated (VI-3) that approximately one-quarter of one percent of the dyes used are not exhausted and are thus discharged to the sewer. Assuming that all of the unreacted benzidine-based dyes would be reduced in the sewer to benzidine, one can estimate that the concentration of benzidine in the wastewater would be raised by 15.86 ppb assuming that approximately 50 percent of the dye molecule is benzidine on a weight basis. While it appears that the potential problem is not a major consequence, the actual magnitude of the problem must be defined through analysis of the wastewaters at S. B. Foot Tanning Company and at other leather processing plants where similar reducing conditions could occur.

Paper: Peninsular Paper Company .... Peninsular Paper Company of Ypsilanti, Michigan produces paper stock that is employed primarily for report covers, photomounts, etc. Although this company is considered to be small by industry standards, it is considered to be a high volume user of Direct Black 38, the only benzidine-based dye it uses in its manufacturing operations. Consequently, this dye applicator can be classified as a "heavy use" situation.

Assuming that the Direct Black 38 used by Peninsular Paper Company contains 20 ppm of benzidine, one can calculate the maximum concentration of benzidine that could be present in their wastewater. Such calculations were conducted for the accounting period which extended from 23 June through 27 July 1975. The calculations which have been tabulated in Table VI-3 show that Direct Black 38 was used only on Fridays. The calculated maximum possible benzidine concentrations in the exhausted pulping liquors ranged from 1.01 to 8.54 and averaged 4.582 ppb on the days when the benzidine-based dye was used. The average calculated total mass discharge of benzidine is 0.0128 pounds per day. The dye was applied at a level of 1.8 percent of the finished weight of paper produced.

Peninsular Paper Company occasionally strips the Direct Black 38 dye from paper which has been recycled. In the past this was achieved either by the reductive stripping method using hydrosulfite or by oxidative stripping using hypochlorite. Because reductive stripping did not yield the desired result, Peninsular Paper Co. now strips only oxidatively.

The wastewaters discharged by Peninsular Paper Co. are transported to the City of Ypsilanti wastewater treatment plant through its gravity flow sewer

TABLE VI-3

CALCULATED MAXIMUM POSSIBLE BENZIDINE CONCENTRATION IN THE WASTEWATERS OF PENINSULAR PAPER CO.

Date	Dye Usage (pounds)	Water Usage (1000's gallons)	Benzidine Conc. (ppb)
6-23-75	0	764.8	0.0
6-24-75	0	329.0	0.0
6-25-75	0	332.8	0.0
6-26-75	0	335.8	0.0
6-27-65	625	324.8	4.61
6-30-75	0	417.6	0.0
7-1-75	0	269.8	0.0
7-2-75	0	305.2	0.0
7-3-75	575	225.8	6.11
7-7-75	0	397.6	0.0
7-8-75	0	234.4	0.0
7-9-75	0	262.8	0.0
7-11-75	750	680.0	2.64
7-14-75	0	360.4	0.0
7-15-75	0	301.0	0.0
7-16-75	0	324.6	0.0
7-17-75	0	253.4	0.0
7-18-75	150	357.0	1.01
7-21-75	0	538.8	0.0
7-22-75	0	282.6	0.0
7-23-75	0	267.4	0.0
7-24-75	0	358.0	0.0
7-25-75	1100	308.6	8.54

network. The plant is a conventional activated sludge biological treatment facility with primary and secondary clarification and anaerobic sludge digestion. The City of Ypsilanti limits Peninsular's discharge only with respect to the volumetric flow. No requirements regarding the discharge of any specific pollutants have been imposed.

Questionaire Survey

To futher evaluate the utility of the mass balance approach for monitoring the wastewaters of benzidine-based dye applicators a questionaire was forwarded to five industries in each of the three industrial categories; paper, textile, and leather. Names and addresses of the 15 industries contacted by telephone and subsequently by letter were supplied by the Benzidine Task Force of the Synthetic Organic Chemicals Manufacturing Association. The questionaire, questionaire information sheet, and supporting documentation have been appended as Appendix C.

Paper .... Five paper manufacturing concerns were asked: (1) to identify that month of the 1974 through 1975 calendar year period during which the firm used the greatest quantity of benzidine-based dyes; (2) to record the quantity of benzidine-based dyes used each day during that month; and (3) to record the quantity of water discharged daily for the same period. All of the five industries contacted responded. Because one of the industries (#3) recycles and reuses its wastewater, the data supplied by it cannot be used for evaluation of the mass balance approach. Nonetheless, this industry (#3) used benzidine-based dyes only one day during the month data base period. On that day a total of 315 pounds of dye were used.

A compilation of the data supplied by the four other paper manufacturers is presented in Table VI-4. The table includes data regarding the discharge concentration and total discharge mass of benzidine on a daily basis assuming that the benzidine-based dyes contain 20 ppm benzidine as an impurity and that all of the free benzidine in the dye is discharged with the wastewater.

The data has been summarized in Table VI-5. The four manufacturers surveyed used benzidine-based dyes on 19, 30, 18, and 2 days during their respective "heavy use" one-month data base period. Average calculated concentrations of benzidine that could have been present in the wastewater were 0.0213, 0.4893,

TABLE VI-4

BENZIDINE DISCHARGED BY FOUR PAPER MANUFACTURERS: MASS BALANCE APPROACH

Day	Industry #1		Industry #2		Industry #3		Industry #4	
	Conc. (ppb)	Disch. Mass (10^{-3}#/day)	Conc. (ppb)	Disch. Mass (10^{-3}#/day)	Conc. (ppb)	Disch. Mass (10^{-3}#/day)	Conc. (ppb)	Disch. Mass (10^{-3}#/day)
1	0.0006	0.06	0.23	0.60	0.0008	0.20	3.19	8.00
2	0.0	0.0	0.56	1.82	0.0016	0.40	0.0	0.0
3	0.0	0.0	0.47	1.24	0.0015	0.40	0.0	0.0
4	0.04	4.2	0.44	1.14	0.0014	0.40	0.0	0.0
5	0.04	4.2	0.34	1.06	0.0018	0.40	0.0	0.0
6	0.0	0.0	0.14	0.50	0.0	0.0	0.0	0.0
7	0.0	0.0	1.95	6.42	0.0	0.0	0.0	0.0
8	0.0014	0.14	1.11	3.36	0.0	0.0	0.0	0.0
9	0.0006	0.06	0.40	1.24	0.0	0.0	0.0	0.0
10	0.0	0.0	0.28	0.94	0.0	0.0	0.0	0.0
11	0.0014	0.14	0.22	0.72	0.0	0.0	0.0	0.0
12	0.0008	0.08	0.76	1.82	0.0016	0.40	0.0	0.0
13	0.0014	0.14	0.32	0.96	0.0072	1.68	0.0	0.0
14	0.0021	0.20	0.45	1.44	0.0214	5.32	0.0	0.0
15	0.0	0.0	0.66	2.24	0.0196	4.78	0.0	0.0
16	0.0014	0.14	0.32	0.84	0.0107	2.82	3.19	8.00
17	0.132	12.8	0.52	1.44	0.0016	0.40	0.0	0.0
18	0.173	17.0	0.81	2.30	0.0017	0.40	0.0	0.0
19	0.0	0.0	1.13	3.24	0.0	0.0	0.0	0.0
20	0.0015	0.14	0.38	1.02	0.0	0.0	0.0	0.0
21	0.0014	0.14	0.41	1.50	0.0	0.0	0.0	0.0
22	0.0014	0.14	0.34	1.26	0.0	0.0	0.0	0.0
23	0.0	0.0	0.22	0.82	0.0	0.0	0.0	0.0
24	0.0	0.0	0.16	0.44	0.0	0.0	0.0	0.0
25	0.0	0.0	0.59	1.60	0.0015	0.40	0.0	0.0
26	0.0	0.0	0.38	1.30	0.0015	0.40	0.0	0.0
27	0.0	0.0	0.24	0.94	0.0016	0.40	0.0	0.0
28	0.0014	0.14	0.38	1.24	0.0015	0.40	0.0	0.0
29	0.0015	0.14	0.22	0.62	0.0017	0.40	0.0	0.0
30	0.0014	0.14	0.25	0.94	0.0016	0.40	0.0	0.0
31	0.0015	0.14	-	-	-	-	0.0	0.0

TABLE VI-5

SUMMARY OF MASS BALANCE APPROACH FOR PAPER, TEXTILE, AND LEATHER MANUFACTURERS

Industry #	# days B used	# days B not used	Avg. B Conc. (ppb)	Avg. B Discharged (10^{-3}#/day)	Max. B Conc. (ppb)	Max. B Discharged (10^{-3}#/day)
			PAPER			
1	19	12	0.0213	2.11	0.1730	17.0
2	30	0	0.4893	1.50	1.9500	6.42
4	18	12	0.0045	1.11	0.0214	5.32
5	2	29	3.1900	8.00	3.1900	8.00
			TEXTILE			
6	20	10	0.2560	1.79	0.3600	2.38
7	7	24	0.1500	0.52	0.1500	0.52
9	20	10	0.4140	2.16	0.6800	3.40
			LEATHER			
12	20	8	0.7305	4.51	1.2900	6.69
14	26	5	0.2738	0.54	0.76	0.98

Notes: (1) B designates benzidine

(2) Average values reported are for days during which benzidine based dyes were used by the industry.

0.0045 and 3.1900 ppb for Industries #1, #2, #4, and #5, respectively. Corresponding calculated average total mass discharges of benzidine were 0.00211, 0.0015, 0.00111, and 0.008 pounds per day. Similarly, maximum possible concentrations of benzidine were calculated as 0.1730, 1.95, 0.0214, and 3.19 ppb for Industries #1, #2, #4, and #5, respectively, while the maximum total mass discharges were determined to be 0.017, 0.00642, 0.00532, and 0.008 pounds per day. By way of comparison, Peninsular Paper Co. showed an average calculated concentration of benzidine of 4.582 ppb and a maximum calculated concentration of 8.54 ppb.

Textile .... Five textile manufacturers were contacted and asked to supply information analogous to that supplied by the paper manufacturers. Of the five, three responded. The data obtained has been compliled in Table VI-6. This data has also been summarized in Table VI-5.

The three manufacturers surveyed used benzidine-based dyes on 20, 7, and 20 days during the one-month data base period. Average calculated concentrations of benzidine that could have been present in the wastewater were 0.256, 0.15, and 0.414 ppb for Industries #6, #7, and #9, respectively. Corresponding calculated average total daily mass discharges of benzidine were o.00179, 0.00052, and 0.00216 pounds. Similarly, maximum possible concentrations of benzidine were calculated as 0.36, 0.15, and 0.68 ppb for Industries #6, #7, and #9, respectively while the maximum possible total mass discharges were determined to be 0.00238, 0.00052, and 0.0034 pounds per day. By way of comparison, Clyde Fabrics, Inc. showed an average calculated concentration of benzidine of 13.32 ppb and a maximum possible calculated concentration of 17.66 ppb.

Leather .... As before, five leather tanners were asked to supply information that could be employed to evaluate the mass balance monitoring approach. Of the five, two responded, two indicated a desire to respond but did not, and one was unwilling to cooperate in the survey. The data obtained for the two

TABLE VI-6

BENZIDINE DISCHARGED BY THREE TEXTILE GOODS MANUFACTURERS: MASS BALANCE APPROACH

Day	Industry #6		Industry #7		Industry #9	
	Conc. (ppb)	Discharge Mass (10^{-3} #/day)	Conc. (ppb)	Discharge Mass (10^{-3} #/day)	Conc. (ppb)	Discharge Mass (10^{-3} #/day)
1	0.0	0.0	0.15	0.52	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.41	2.04
4	0.0	0.0	0.0	0.0	0.32	1.62
5	0.36	2.24	0.0	0.0	0.60	3.00
6	0.31	2.24	0.15	0.52	0.48	2.42
7	0.33	2.24	0.0	0.0	0.58	2.90
8	0.36	2.24	0.0	0.0	0.0	0.0
9	0.35	2.24	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.13	0.66
11	0.0	0.0	0.15	0.52	0.68	3.4
12	0.12	1.4	0.0	0.0	0.38	1.76
13	0.21	1.4	0.0	0.0	0.27	1.34
14	0.21	1.4	0.0	0.0	0.42	2.10
15	0.21	1.4	0.0	0.0	0.0	0.0
16	0.26	1.4	0.15	0.52	0.0	0.0
17	0.0	0.0	0.0	0.0	0.50	2.52
18	0.0	0.0	0.0	0.0	0.57	2.84
19	0.17	1.14	0.0	0.0	0.55	2.76
20	0.14	1.14	0.0	0.0	0.60	3.00
21	0.16	1.14	0.15	0.52	0.10	0.50
22	0.16	1.14	0.0	0.0	0.0	0.0
23	0.22	1.14	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	0.0	0.33	1.66
25	0.0	0.0	0.0	0.0	0.51	2.56
26	0.35	2.38	0.15	0.52	0.42	2.10
27	0.30	2.38	0.0	0.0	0.40	2.00
28	0.27	2.38	0.0	0.0	0.39	1.96
29	0.31	2.38	0.0	0.0	0.0	0.0
30	0.32	2.38	0.0	0.0	0.0	0.0
31	-	-	0.15	0.52	-	-

who responded has been compiled in Table VI-7 and summarized in Table VI-5.

The two manufacturers surveyed used benzidine-based dyes on 20 and 26 days during the one-month data base period. Average calculated concentrations of benzidine that could have been present in the wastewater were 0.7305 and 0.2738 ppb for Industries #12 and #14, respectively. Corresponding calculated average total daily mass discharges of benzidine were 0.00451 and 0.00054 pounds. Likewise, maximum possible concentrations of benzidine that could have occurred during the period were determined to be 1.29 and 0.76 ppb for Industries #12 and #14, respectively, while the maximum possible total mass discharges were calculated to be 0.00669 and 0.00098 pounds per day. Again, by way of comparison, S. B. Foot Tanning Company showed an average calculated concentration of benzidine of 0.25 ppb.

Analytical Surveys

To provide additional data regarding the possibility of the discharge of benzidine by dye applicators at relatively high levels, the Benzidine Task Force of SOCMA conducted an analytical survey (VI-4) on the wastewaters of a plant which is representative of each of the three industrial categories. These analytical surveys are summarized in the following paragraphs.

Paper .... During the period in which a twenty-four hour composite sample was collected at a paper industry, one of four processing lines was using the benzidine-based dye, Direct Black 38. The other three lines were using non-benzidine based colors. Prior to discharge the plant's wastewater was chlorinated and was clarified using the coagulants aluminum sulfate and lime. Approximately half of the six million gallon per day effluent stream was recycled back to the processing lines after treatment. Analysis of the sample which was taken after the wastewater treatment system showed that no benzidine was detectable using the Chlormaine-T procedure (detectable limit is 10 ppb).

Leather .... Two plants that are representative of the leather industry

TABLE VI-7

BENZIDINE DISCHARGED BY TWO LEATHER MANUFACTURERS: MASS BALANCE APPROACH

Day	Industry #12		Industry #14	
	Conc. (ppb)	Discharge Mass (10^{-3} #/day)	Conc. (ppb)	Discharge Mass (10^{-3} #/day)
1	0.0	0.0	0.20	0.38
2	0.0	0.0	0.25	0.50
3	0.44	2.89	0.76	0.76
4	0.64	4.18	0.16	0.32
5	0.40	2.79	0.0	0.0
6	0.46	3.00	0.40	0.82
7	0.49	3.27	0.29	0.60
8	0.0	0.0	0.26	0.48
9	0.0	0.0	0.24	0.50
10	0.88	5.42	0.41	0.76
11	0.13	0.86	0.04	0.08
12	0.86	6.09	0.0	0.0
13	1.08	6.69	0.0	0.0
14	0.63	3.48	0.03	0.08
15	0.0	0.0	0.26	0.46
16	0.0	0.0	0.10	0.32
17	0.93	5.88	0.28	0.64
18	0.42	2.94	0.24	0.48
19	0.72	4.88	0.0	0.0
20	0.82	5.88	0.05	0.10
21	1.14	5.30	0.16	0.38
22	0.0	0.0	0.51	0.98
23	0.0	0.0	0.28	0.66
24	0.73	3.26	0.37	0.80
25	0.80	5.72	0.13	0.30
26	0.80	5.48	0.0	0.0
27	0.95	6.16	0.23	0.58
28	1.29	6.10	0.31	0.68
29	-	-	0.46	0.94
30	-	-	0.39	0.80
31	-	-	0.31	0.58

were sampled. The discharge from one of the plants totaled approximately one million gallons per day and received no treatment other than simple clarification prior to discharge to a municipal sewerage system. At the time when the composite sample was collected, the benzidine-based dyes Direct Blue 6, Direct Black 38, Direct Red 37, Direct Green 1, Direct Green 6, Direct Blue 2, and Acid Red 85 were being used in the leather processing system. The Chloramine-T procedure again showed no detectable benzidine (less than 10 ppb).

In the other leather processing plant that was sampled the benzidine-based dyes that were used at the time of sampling included Direct Black 38, Erie Brown 3GN, Erie Catechine 3G, and Erie Scarlet B. Other dyeings using Buffalo Black NBR, a non-benzidine-based dye, were being made at the same time. The plant's discharge of 200,000 gallons per day was treated by primary sedimentation and the extended aeration process prior to discharge. As before, analyses of the composited sample showed no detectable benzidine.

Textiles .... A textile mill whose primary product was upholstery also was surveyed. During the sampling period the benzidine-based dye used was Erie Black GXR. Other dyeings made during the sampling period included the dyes Niagara Blue 2B, Erie Yellow Y, Erie Green MT, and Solantine Brown BRL. This mill's effluent (700,000 gallons per day) was discharged directly into a municipal sewerage system. Grab samples of the final effluent which were taken on two-hour intervals and were composited over a 24-hour period showed no detectable traces of benzidine using the Chloramine-T procedure (less than 10 ppb).

POTENTIAL REDUCTION PROBLEMS

If strong reducing conditions exist, benzidine-based dyes may be reduced to the parent compound, benzidine. Generally, two possibilities for such reduction exist in the plants of dye applicators.

(1) Paper, leather, and textile producers commonly strip dyes from product materials that did not meet quality control standards.

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POTENTIAL REDUCTION PROBLEMS

If strong reducing conditions exist, benzidine-based dyes may be reduced to the parent compound, benzidine. Generally, two possibilities for such reduction exist in the plants of dye applicators.

(1) Paper, leather, and textile producers commonly strip dyes from product materials that did not meet quality control standards.

These materials are then recycled for reprocessing. Such stripping operations can be accomplished either oxidatively or reductively.

(2) Reducing materials such as hydrosulfite may be used in textile, paper, or leather processing operations that are not associated with dye application itself. The dehairing operation at S. B. Foot Tanning Company, mentioned earlier, is an example of such an operation. If the reducing agents are discharged to the process sewer where they may combine and mix with exhausted dye liquors, then the break-down of benzidine-based dyes in the dye liquors to benzidine could occur.

The Benzidine Task Force of SOCMA has attemped to eliminate the first of the two potential problems by instructing their respective clients to strip oxidatively and not reductively. Copies of such instructive notifications that are being transmitted by Allied Chemical Company and GAF Corporation have been included as Appendix D.

Of the five paper, three textile, and two leather manufacturers that responded to the questionaire survey, two indicated that they did dtrip benzidine-based dyes reductively. All others did not. One, a paper manufacturer, strip such dyes seven days per month at the rate of 10,000 pounds per day. The other, a carpet manufacturer, indicated that an average of one beck bond of carpet per month would be stripped. This requires approximately 80 pounds zinc formaldehyde sulfoxylate.

No similar efforts have to the knowledge of the writer been made to date to eliminate the second possibility. To establish the potential magnitude of the problem all survey respondents were queried regarding their use of reducing agents. Their responses have been tabulated in Table VI-8. In general, the daily quantity of reducing agents used by any of the respondents is substantially less than that used by the S. B. Foot Tanning Company. Nonetheless, because

TABLE VI-8

USE OF REDUCING AGENTS BY BENZIDINE-BASED DYE APPLICATORS

Industry ID #	Use (Yes/No)	Avg. Monthly Usage (pounds)	Maximum Daily Usage (pounds)	Reason For Use
		PAPER		
1	Yes	975	190	pulp brightener
2	Yes	875	125	neutralizer
3	No	-	-	-
4	Yes	1000	35	chlorine reduction
5	No	-	-	-
		TEXTILE		
6	Yes	8000	600	clear dyes
7	Yes	1214	270	strip tint
9	Yes	250	20	clean equipment
		LEATHER		
12	No	-	-	-
14	No	-	-	-

no actual data regarding the in-situ production of benzidine is currently available, this potential pathway should be extensively investigated to ensure that excess concentrations of benzidine do not result from the reduction of benzidine-based dyes that are contained in the exhausted dye liquors.

SUMMARY

Based on the data presented above, it appears that the mass balance monitoring approach could be entirely satisfactory for use by dye applicators. If this procedure is adopted, however, it is imperative to show either that benzidine-based dyes are not reduced to benzidine under the reducing conditions that might be encountered in the wastewaters of dye applicators or, if reduction does indeed occur, that the maximum possible benzidine concentration meets the discharge limits. Otherwise, a chemical analytical procedure would be the only alternative.

It is important to note also that most dye applicators either own and operate a biological wastewater treatment system (aerated lagoon or extended air activated sludge) or discharge into a municipally owned one. Since it has been demonstrated that biological treatment will remove approximately 90 percent of benzidine in wastewater if the influent concentration is less than 50 ppb, the concentrations of benzidine discharged to the environment by dye applicators would, therefore, be expected to be extremely small. In essence, the bio-treatment systems would provide an added margin of safety.

LITERATURE CITED

VI-1	K. H. Ferber, Trip Report, 7-29-75
VI-2	W. M. Reiter, Trip Report, 7-29-75
VI-3	D. Waite, Trip Report, 8-5-75.
VI-4	Anon. "Survey of Benzidine in Effluents from Dye Users" Benzidine Task Force, SOCMA, July 1974.

APPENDIX

A

INDUSTRIAL HYGIENE & ENVIRONMENTAL CONTROL
EMPLOYED BY THE
BUFFALO DYE PLANT

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INDUSTRIAL HYGIENE & ENVIRONMENTAL CONTROL

The operating, maintenance, and control practices related to the industrial hygiene program for benzidine are set forth in the SCD Industrial Hygiene Guideline No. 4. The purpose of the guideline is to assure no retrogression in standards or procedures which are designed to guarantee safe working conditions.

Safe exposure levels in the manufacture of benzidine depend on a few basic factors:

1. Manufacture and use only of aqueous benzidine sulfate slurry which eliminates both dust and vapor and permits mass transfer within a closed system until entirely converted to benzidine tetrazo.
2. Filtration, washing & discharge of the benzidine sulfate by means of a closed Valle' filter which can be decontaminated before periodic replacement of screens or other maintenance.
3. Wet decontamination of any and all items of equipment by operating personnel before maintenance application.
4. Establishment of control standards for air, clothing, equipment, and building based on best past performance with periodic revision toward tighter control.
5. Education and training of foremen and workers in the nature of the hazard and the necessity for adherence to rules and good housekeeping.
6. Insistence on good housekeeping backed up by periodic self-inspections as well as periodic management inspections.
7. Seeking and locating the cause of excursions in environmental levels of benzidine, followed by corrective measures.
8. Well-engineered ventilation.

The proof of effectiveness of the above measures can be demonstrated only over time. As pointed out, there have been no tumors among workers exposed only in the last 19 years.

K. H. Ferber

K. H. Ferber
5/30/75

KHF:dmw

ALLIED CHEMICAL CORPORATION
SPECIALTY CHEMICALS DIVISION
INDUSTRIAL HYGIENE GUIDELINE NO. 4
ISSUED: JUNE 14, 1974

1. Subject: Benzidine Sulfate

2. Background Information:

Benzidine and its salts have long been recognized as a human bladder carcinogen. The cases which have occurred among Buffalo Dye Plant workers all involve exposure to the early process and operations. These operations were carried out in open processing equipment, and included hand cleaning of plate and frame filter presses, molten phase separations of benzidine base, distillation and flaking with high dust and sublimate levels. New manufacturing facilities, a catalytic reduction process, elimination of all base operations and institution of a variety of process and administrative controls have drastically reduced exposure levels. No new cases have occurred among those workers whose only exposure has been to the latest process and equipment commissioned in 1955. The nature of the risk is such, however, that exposure must be maintained at the lowest practicable limit through the promulgation and enforcement of administrative, engineering and processing controls, and industrial hygiene practices.

It is the purpose of this guideline to assemble the existing rules, procedures, policies and controls for ready reference and guidance as well as to furnish a point of departure for future improvements.

In September 1972, representatives of NIOSH inspected the benzidine and benzidine tetrazo plants and followed with a report on their findings and recommendations which were promptly implemented. For the most part, these recommendations have been included in this guideline.

In December 1972, at Allied's request, Dr. Ralph G. Smith of the University of Michigan examined the benzidine plant and related health controls and made additional recommendations which were implemented and have also been included in this guideline.

On May 3, 1973, OSHA promulgated an emergency temporary standard on certain carcinogens, including benzidne sulfate. The Buffalo Dye Plant promptly developed an action plan to bring the production and use facilities into compliance with the standard. This plan will be fully executed following installation of certain necessary equipment in 1974.

2. Background Information: (Cont'd.)

On December 5, 1973, Mr. Margolies of the Industrial Hygiene Division of the N. Y. State Department of Labor inspected the benzidine facilities and found our handling of the occupational health aspects to be satisfactory.

On February 11, 1974, following deliberations by a standard advisory committee, public hearings and written testimony, OSHA issued permanent occupational and health standards for carcinogens including benzidine sulfate. A copy of the pertinent sections is attached as a part of this guideline (Appendix F).

On December 27, 1973 (Fed. Reg. 38 (247) 35-388-35395, Part II), the Environmental Protection Agency published Proposed Toxic Pollutant Effluent Standards covering nine pollutants, including benzidine and its salts. Public hearings are scheduled for April 1974. Various studies of the fate of benzidine in the environment have been initiated by Allied to assist the EPA in the development of a safe and practicable standard. The Synthetic Organic Chemicals Manufacturers Association (SOCMA) is representing industry at the forthcoming hearings.

In 1973, The International Labour office issued Report VII (2) on Control and Prevention of Occupational Cancer. The proposed conclusions have been given serious consideration and these guidelines are in accord with the principles set forth in the report.

3. Policy:

.1 The regulations of OSHA as set forth in the Federal Register of Jan. 29, 1974, Vol.39, No. 20 Part III pp 3756-3797 shall be followed in all respects unless exceptions on variances thereto have been obtained through Allied Legal.

.2 No individual (worker, supervisor or visitor) is to be knowingly exposed to benzidine or its salts at concentrations or under conditions that are not in conformance with these guidelines.

.3 The number of workers assigned to the maintenance of benzidine sulfate and to the manufacture of equipment and lines used in the benzidine process shall be kept as low as practicable. Rotation of personnel into and out of the benzidine assignments shall not be permitted.

3. Policy: (Cont'd.)

.4 Within the limitation of contractual agreements, older replacements are to be selected over younger men in order to limit the potential induction period.

.5 Maintenance or construction tradesmen are to work only on decontaminated equipment.

.6 A preventive maintenance schedule should be developed and executed based on past experience and engineering calculations.

.7 Unanticipated maintenance on processing equipment or hygiene accessories shall be given high priority of attention.

.8 It shall be a condition of employment that benzidine workers conform to all rules and procedures, including personal hygiene and protective measures.

.9 The working atmosphere, equipment and building surfaces shall be regularly monitored and minimum standards shall be developed and applied. Failures to meet the standards shall prompt immediate investigation and corrective action.

.10 Biological monitoring shall be carried out and results made available to the workers involved. Abnormal readings shall result in prompt medical evaluation and appropriate further diagnosis and therapy. Each test result shall be filed in the respective individual's permanent medical record file.

.11 Benzidine or its salts shall be manufactured, handled and consumed in bulk quantities only at the Buffalo Dye Plant. Laboratory quantities may be furnished to Divisional or Corporate Research upon request of a section manager.

.12 All location medical case records shall be maintained in readily retrievable form for at least 20 years or the lifetime of the employee or retiree, whichever is the longer period.

.13 Effluents containing benzidine shall be monitored and a standard established for maximum discharge to city sewers which will represent best practicable performance consistent with proposed or effective EPA standards. All effluents containing benzidine shall be handled in a manner that will prevent direct discharge into streams. Building and equipment washdowns or spillages shall not be allowed to drain directly to sewers but shall be collected and decontaminated before release to process waste sewers. (See Appendix J)

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3. Policy: (Cont'd.)

.14 Process emissions shall be cleaned before release to the atmosphere. Stack standards shall be developed based on good practice and subject to regular monitoring control.

.15 Contaminated solid wastes shall be decontaminated before removal from the manufacturing or using areas.

4. Guidelines:

.1 The purchase, handling, use or manufacture of benzidine base or benzidine dihydrochloride is prohibited except by Divisional or Corporate Research after approval by the Director.

.2 The manufacture, handling, transportation and use of benzidine sulfate shall be restricted to a pumpable slurry handled in closed equipment.

.3 Benzidine Sulfate shall not be sold without specific approval of the Divisional president.

.4 Samples of benzidine shall be sent out only under the supervision of the Technical or Research & Development Departments. Except under direct technical supervision, samples shall be obtained by use of a ventilated glove box.

.5 Operating instruction manual, standard process, product specification, testing methods and decontamination procedures shall be kept up-to-date and include explicit reference to the nature of the hazard and necessary precautions.

.6 Access to manufacturing or use areas shall be restricted to authorized personnel and appropriate signs to the effect shall be posted at building entrances or area limits. A log of time of entry and exit by individuals shall be maintained as a permanent record of the Safety Department.

.7 Operating personnel shall decontaminate equipment, containers and solid wastes before maintenance application or removal. Decontaminated surfaces are those that contain less than $0.02\ mg/m^2$ of benzidine (calc. as base) according to Standard Testing Method SP 125 Suppl. or its equivalent. Cases of doubt should be referred to the Superintendent of Safety.

4. Guidelines: (Cont'd.)

.8 All workers and supervisors assigned to benzidine manufacture, maintenance or use shall be informed of the nature of the hazard and required precautions as prescribed in this guideline and in local rules and procedures. These communications shall be made a matter of record by the Safety Department.

.9 A special "street and work" locker room shall be used in Bldg. 54 to assure that potentially contaminated clothing will not be worn or taken from the manufacturing area. Rules and procedures shall be posted.

.10 Hourly personnel assigned to operate or maintain the benzidine sulfate process in Bldg. 54, the transfer of slurry to Bldg. 115 or the conversion to benzidine tetrazo shall wear only freshly laundered work clothing each day. Gloves shall be replaced on a daily basis. Shoes, hats and bootees shall be replaced in accordance with current practice and agreements, except as otherwise determined by the Foreman and the Safety Department.

.11 Eating in the operating area of Bldg. 54 or in consuming areas is not permitted. Smoking is allowed only at designated times in specified areas. Food may be eaten only in the Street side of the Street and Work Locker room. Rules shall be posted.

.12 Employees who are scheduled for the first time for regular assignment to actual operations or actual maintenance in Bldg. 54 or on the Benzidine Tetrazo process in Bldg. 115 will meet with the Technical Manager or his designated representative, prior to the commencement of work, to discuss the procedures necessary to protect themselves from exposure to benzidine sulfate slurry. The Company will make every effort to minimize replacement of personnel in these areas in order to maintain at the lowest possible level the cumulative number of individuals assigned.

.13 Each operating and maintenance workman assigned regularly or on a special basis to either the benzidine sulfate or benzidine tetrazo processes is required to take a shower at the end of his shift.

4. Guidelines: (Cont'd.)

.14 Soiled clothing from benzidine operations or maintenance shall be laundered separately from regular plant laundry following a written decontamination procedure provided by the Plant Technical Dept. Periodic, random samples shall be taken of both soiled and freshly laundered clothing to ascertain the degree of contamination, if any, and the efficiency of the laundering operation using Std. Testing Method SP 125 Supp IV (See Appendix D) or equivalent.

.15 Those individuals judged by the Safety Dept. to have been significantly exposed in the past, shall be listed and requested to have cystoscopic examinations at intervals recommended by their chosen urologist. This list shall distinguish between those having at least one positive diagnosis and those who have had only negative diagnoses. Personnel whose only exposure to the benzidine sulfate or benzidine tetrazo processes has been subsequent to Jan. 1, 1959, will not be required to have cystoscopic examinations as a condition of the job assignment. Cystoscopic examination at Company expense will be optional, however, at whatever frequency is recommended by the selected urologist.

.16 At least once every six months and at such shorter intervals as may be recommended by the employee's urologist, Papanicolaou urinalysis shall be carried out on each present or former employee or retiree regularly assigned for more than one month to benzidine operations or maintenance. Corporate records of the results shall be maintained by the Medical Dept. and made available to the tested individual. Other may have access to the records only on a "need to know" basis. In the event that urinalyses disclose the possibility of neoplastic changes, the individual concerned will be so advised and requested to undergo cystoscopic examination including an intravenous pyelogram. The recommendation of the urologist will determine whether said individual will then be "listed" (4.15 above) or continue under the urinalysis protocol. Urinalyses for benzidine using Std. Testing Method SP-194 Rev. (See Appendix E) shall be performed semi-annually on currently assigned operating and routine maintenance workers using samples collected at the end of the work shift.

4. Guidelines: (Cont'd.)

.17 The atmosphere in both manufacturing and use areas shall be sampled at critical working locations at least semi-monthly and analyzed for benzidine content by Std. Testing Method SP-152 Rev. 1 (See Appendix C). Unless superseded by more stringent OSHA standards, a single test result in excess of .000060 mg/m^3 (60 nanograms/m^3) or a mean of ten consecutive results in excess of .000050 mg/m^3 (50 ng/m^3) shall be cause for immediate investigation as to probable cause and required corrective action in Bldg. 54. In the consuming areas the single test standard shall be .000125 mg/m^3 (125 ng/m^3) pending accumulation of sufficient data to evaluate best performance.

.18 Sludge from the Buffalo Dye Plant waste water treatment plant shall be analyzed at least weekly for benzidine content according to Std. Testing Method No. 187 Rev. 3 (See Appendix L). Standard should be based on best past performance (95% upper quality control point) and test results above such standard should invoke immediate investigation and corrective action.

.19 A 24-hour average sample of the discharge of treated waste water to Buffalo City Sewers shall be taken at least weekly and analyzed by Std. Testing Method No. SP 222 Rev. (See Appendix H). Standard should be based on best past performance (95% upper quality control point) and test results above such standard should invoke prompt investigation and corrective action.

.20 The equipment, accessories, vent ducts, lines, walls and floors of the manufacturing and use areas shall be sampled at least monthly and analyzed for benzidine content by Std. Testing Method SP-125 Suppl. I Rev. or SP-125 Suppl. II Rev. (See Appendices B1 & B2) Any result in excess of 0.10 mg/m^2 shall be cause for immediate decontamination of the surface in question until repeat tests indicate a level below 0.02 mg/m^2. High results for any item should activate a survey of other areas to assure that the contamination is not widespread.

.21 Periodic wipe tests shall be made of hats, shoes, goggles, gloves, glove boxes, lockers and other accessories with which workers may be in regular contact. STM SP 125 Suppl. I Rev., Suppl. II Rev. and Suppl. III are applicable (See Appendices B1, B2 and K) Standards should be based on best past performance (95% upper quality control point) and test results in excess of such standard should invoke immediate investigation and corrective action.

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4. Guidelines: (Cont'd.)

.22 No items of equipment shall be removed from their locations for replacement or repair until the surfaces have been tested and found to have less than 0/02 mg/m^2 of benzidine.

.23 Separate "street and work" locker rooms shall be provided for "clean" or street clothing and for "current use" or work clothing, including work shoes. The lockers shall be separated by a shower room. Rules for use of the locker rooms and showers shall be posted.

.24 Benzidine workers shall change to clean clothes and wash hands, face, neck & arms before leaving the manufacturing building or regulated area for lunch or other reason.

.25 Whenever a major spill, emergency equipment cleanout or unusual maintenance job involves risk of abnormal exposure to benzidine sulfate, the workers at risk shall be monitored for urinary benzidine before and after their work period. The method shall be at least as sensitive as Standard Testing Method SP-194. Any result in excess of .025 mg/l of benzidine in urine is considered excessive and steps must be taken to reduce potential exposure before work is resumed or repeated in kind.

.26 During production operations including transfer of benzidine sulfate, the entire Bldg. 54 (except "street" locker room) shall be designated as the regulated area subject to OSHA regulations. When that portion of the process involving the formation, treatment and transfer of benzidine sulfate is not in operation, the regulated area shall not normally change except for unusual planned maintenance or construction on the building or on vessels not containing benzidine sulfate during which such temporary activity, the regulated area may be considered to be limited to the closed vessels and accessory equipment providing the work area has been tested and found to be passable vs. standards described in these guidelines.

.27 Inflowing building air shall be filtered and filters maintained in satisfactory working condition. The incoming air after filtration shall not exceed 0.000010 mg/m^3 of quinonizable amines as benzidine. Building and equipment exhaust air shall be collected and cleaned by wet scrubbing. The exit air shall not exceed 0.000020 mg/m^3 of benzidine or such stricter standard as may be imposed by a regulatory agency. The scrubber shall be equipped with signals or alarms to indicate that fans are running and adequate differential pressure being maintained at all times while the process is operating.

4. Guidelines: (Cont'd.)

.28 A self-inspection checklist should be prepared and used at least monthly by the Operating Dept. to guide self-inspections of both producing and consuming areas. In addition, a thorough and comprehensive inspection should be conducted at least twice each year by a special panel of technical personnel. This inspection should include the entire transfer line. Recommended corrective measures should receive high priority of attention.

.29 It is important to maintain a high standard of psychological factors which contribute to good manufacturing practice, enthusiasm and morale. Adequate and well-maintained lighting, clean and frequently painted equipment and service lines, labeled lines, regularly cleaned windows and adequate storage facilities are examples of the factors in question.

.30 Laboratory operations involving benzidine sulfate shall be confined to hoods in accord with OSHA regulations and specifications. Unused portions of samples should be returned to the operating department or chemically destroyed within one month. Temporary storage should be in sealed & labeled containers kept inside of a hood. Laboratory workers shall wash face, neck, hands & arms after completion of the hood operations.

.31 Any problems associated with the application of these guidelines should be brought to the immediate attention of the appropriate local department head or plant manager.

5. Appendices:

A. pp 40 & 41 of Threshold Limit Values with Intended Changes for 1973 - ACGIH.

B1. STM-SP 125 Suppl. I Rev. (3/13/72)

B2. STM-SP 125 Suppl. II Rev. (5/16/74)

C. STM-SP 152 Rev. (5/9/74)

D. STM 125 Suppl. IV (1/29/74)

E. STM-SP-194 Rev. (4/20/73)

F. OSHA Standard for Carcinogens (Fed. Reg. 39 (20) 3756-3760, 3779-81, 3797 (1/29/74).

5. Appendices: (Cont'd.)

G. EPA Proposed Toxic Pollutant Effluent Standard (Fed. Reg. 38 (247) 35388-35391 (12/27/73))

H. STM SP-222 Rev. (1/15/74)

J. Tech. Report File No. 134: Decontamination of Benzidine Filtrates and Washes, R. A. Mazur (5/2/74)

K. STM SP-125 Suppl. III (11/15/73)

L. STM SP-187 Rev. 3 (6/15/72)

6. Selected Literature References:

.1 Ferber, K. H. "Industrial Bladder Cancer" A Progress Report and Some Unanswered Questions". J. Nat'l. Canc. Inst. 43 (1) 245-248 (1969).

.2 Goldwater, L. J. Rosso, A. J. & Kleinfeld, M., "Bladder Tumors in a Coal Tar Dye Plant" - Arch. Environ. Health 11, 814-817 (1965).

.3 Gadian, T., "Industrial Cancer" Fourth Symposium on Chemical Process Hazards with Special References to Plant Design - The Institution of Chemical Engineers - North Western Branch - Umist., Manchester April 6, 1971.

.4 British Ministry of Labour - Statutory Instruments 1967 No. 879 - The Carcinogenic Substances Regulations 1967.

.5 Chester Beatty Research Institute, Royal Cancer Hospital London, England: "precautions for Laboratory Workers who handle Carcinogenic Aromatic Amines". April 1966.

.6 Scott, T. S. & Williams, M. H. C. - "The control of Industrial Bladder Tumours". Brit. J. Industrial Med. 14, 150-163 (1957).

.7 Int'l Agency for Research on Cancer-Monograph on the Evaluation of Carcinogenic Risk of Chemicals to Man Vol. 1 WHO 1972.

.8 Int'l Labour Office - Control and Prevention of Occupational Cancer - Report VII (2) - ILO Conference - 58th Session 1973.

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7. APPROVALS: Kelvin H. Fisher
Manager - Environmental Control

June 7, 1974
Date

R. Sobel
Director of Environmental and Process Technology

June 12, 1974
Date

8. Initial Distribution:

W. S. Ferguson, R. Sobel, J. C. Bishop, E. C. Bailey (3), W. C. Parle, M. Saltzman, File 6.6.6.2.4 (2), FILE 6.7.1 (2)
G.F. LISK, FILE 6.16.2.1, [illegible]

KHF:dmw

Attach.

APPENDIX

B

CHLORAMINE T PROCEDURE FOR BENZIDINE DETECTABILITY LIMITS

DETECTABILITY LIMITS FOR BENZIDINE

(CHLORAMINE T PROCEDURE)

Matrix	Detectability Limit
Clear Stream Waters	0.1 ppb
Wastewater Treatment Plant Effluent	0.2 ppb
Primary Clarifier Effluent	0.2 - 0.5 ppb
Raw Wastewater	2 - 5 ppb
Nitrous Acid Treatment Effluent	10 - 20 ppm/10 ppb

APPENDIX

C

MASS BALANCE QUESTIONAIRE SURVEY

QUESTIONAIRE INFORMATION SHEET

EPA Benzidine-Based Dye Usage Survey

Introduction

Benzidine is a well known cancer causing agent that can cause bladder tumors. It is for this reason that benzidine has come under the toxic pollutant discharge standards that currently are being promulgated by the Environmental Protection Agency.

Certain dyes are produced using benzidine as a raw material. As in any chemical reaction a certain quantity of the benzidine remains unreacted in the dye mixture. That is, benzidine is an impurity in the dye just as mercury can be an inpurity in caustic. Manufacturers of benzidine-based dyes certify that their dye products contain no more than 20 ppm of benzidine. Generally, however, the dyes contain no more than 5 to 10 ppm of benzidine. These levels have been judged to be "extremely safe" from the worker exposure/health standpoint.

For the protection of drinking water supplies and aquatic life, however, the EPA has proposed a standard of 125 ppb (0.125 ppm) for wastewaters that are discharged either directly to receiving waters or to publically-owned treatment works. Dye applicators would meet these proposed standards if the benzidine in the benzidine-based dyes were diluted 100-fold as the dyes were used in the plant. Several heavy dye applicators whose plants I personally visited have dilution ratios of one to two-thousand. That is, the concentration of benzidine in their discharges averaged 0.25 to 10 ppb (500X to 12.5X below the proposed discharge standard). It is noteworthy, that the plants visited included a paper mill, a textile mill, and a leather tanning plant.

Even though it now appears that all dye applicators likely are in compliance with the proposed standard for benzidine, the EPA originally proposed that all benzidine-based dye applicators be required to analytically monitor their effluents to ensure that their discharges were in compliance with the standards. Such monitoring, however, is an expense that probably is unwarranted in light of the low concentration levels of benzidine that were subsequently found in the wastewaters of selected dye applicators' manufacturing facilities. Based on this new evidence the EPA decided that a "mass balance" monitoring approach could serve to ensure protection of the environment and compliance with the standard.

The "mass balance" monitoring approach requires the use only of inventory records: i.e., knowing how many pounds of benzidine-based dyes were used during a particular time period and knowing the total quantity of water discharged from the plant during the same time period, one can calculate the maximum concentration of benzidine that could possibly be present in the wastewater assuming that 20 ppm of benzidine is present in the dye and that all of it is discharged into the wastewater. The "mass balance" or inventory monitoring approach certainly is more economical than an analytical monitoring approach which would require routine sampling and analysis and the acquisition of relatively sophisticated analytical instrumentation.

If the "mass balance" approach is to be adopted, however, it is important to show prior to adoption that the concentrations of benzidine that could be present in the wastewaters of dye applicators is materially less than the proposed standard (125 ppb). Accordingly, an appropriate data base is required. It is in this context that your assistance is being solicited.

Data Base Required

To evaluate the maximum likely concentration of benzidine that could be contained in the wastewaters of dye applicators I am asking you and fourteen other manufacturing concerns (five representatives each for the paper, leather, and textile industries) to survey your inventory records for the calendar years 1974 and 1975 and identify that month of the two-year period during which your firm used the greatest quantity of benzidine-based dyes. Please refer to the attached lists provided by Allied Chemical Corporation and GAF Corporation if you are in question as to which dyes and dye mixes are benzidine-based.

After having identified the heavy-use month, then record on the attached data sheet the quantity (pounds) of benzidine-based dyes used each day during that month. For the same period record the quantity of water discharged daily by the plant. If you do not have the water usage information readily available, please feel free to use your best estimate for water flows.

Two additional questions regarding the use of sodium hydrosulfite or similar reducing agents have also been included on the questionaire. These have been included to assess the potential for the possible reduction of benzidine-based dyes in the presence of strong reducing agents to benzidine itself. Please answer these questions to the best of your knowledge.

Confidentiality

The data that you are providing will be presented for the record at a hearing regarding the toxic pollutant effluent standards for benzidine. It will be employed to support the case for using the "mass balance" approach for monitoring the wastewaters of dye applicators in lieu of the analytical approach. This, of course, is extremely beneficial to your cause.

You will note that the questionaire has been given an identification number. All disclosures of your data will be made only with reference to that identification number. No other identification will be made. I, and I alone, will hold the key which identifies the industrial firms surveyed with the ID code number. This key will be disclosed to no one, period.

Survey Distribution

Upon completion of the survey you will be provided a copy of summarized data tabulated by ID code number for all of the industries surveyed. This is for your information and future reference.

Thomas M. Keinath, Ph.D.
Route #2, Box 272-A
Seneca, South Carolina 29678

Home: 803/654-2992
Office: 803/656-3276

QUESTIONAIRE

Usage of Benzidine-Based Dyes

(Survey for the Environmental Protection Agency)

* * * Identification No.______________ * * *

I. Benzidine-Based Dye Usage

(A) For the heaviest benzidine-based dye usage month which occurred during either the 1974 or 1975 calendar years tabulate below the quantity of dye used daily and the corresponding quantity of process water used by the entire manufacturing facility.

Date (day)	Quantity of Benzidine-Based Dyes Used (pounds/day)	Quantity of Water Used (gallons/day)	Date (day)	Quantity of Benzidine-Based Dyes Used (pounds/day)	Quantity of Water Used (gallons/day)
1	________	________	16	________	________
2	________	________	17	________	________
3	________	________	18	________	________
4	________	________	19	________	________
5	________	________	20	________	________
6	________	________	21	________	________
7	________	________	22	________	________
8	________	________	23	________	________
9	________	________	24	________	________
10	________	________	25	________	________
11	________	________	26	________	________
12	________	________	27	________	________
13	________	________	28	________	________
14	________	________	29	________	________
15	________	________	30	________	________

(B) Month and Year of Data Base: ________/____________
month year

II. Does your manufacturing facility use sodium hydrosulfite or a similar reducing agent? ☐ Yes; ☐ No. If the answer is yes, (1) what quantity would be used during an average month, ______ pounds/month; (2) what quantity would be used during a maximum use day, ______ pounds/day; and (3) for what purpose is the reducing agent employed, ____.

III. Does your manufacturing facility reductively strip any of the benzidine-based dyes (listed on the attachments) from dyed material or goods using either sodium hydrosulfite or a similar reducing agent? ☐ Yes; ☐ No. If the answer is yes; (1) how frequently do you do so (please give narrative statement) ____.

(2) What quantity of material would be stripped during an average month, ________ pounds/month; and (3) what quantity of material would be stripped during a maximum (stripping) day ________ pounds/day.

G A F CORPORATION

BENZIDINE DYES

PRIMARY BENZIDINE DYES:

Phenazo Black BH	Direct Blue 2
Phenazo Black BH 50	Direct Blue 2
Phenazo Black BH 150	Direct Blue 2
Phenamine Blue BB Conc	Direct Blue 6
Phenamine Blue BBN	Direcet Blue 6
Supranol Red PG Extra	Acid Red 85
Supranol Red PRX	Acid Red
Paper Scarlet 3BP	Direct Red 39
Paper Scarlet BP	Direct Red 37
Phenamine Scarlet B	Direct Red 37
Phenamine Fast Red F	Direct Red 1
Paper Orange R	Direct Org 8
Phenamine Green G	Direct Green 6
Phenamine Green BG	Direct Green 6
Phenamine Black E	Direct Black 38
Phenamine Black E 200	Direct Black 38
Phenamine Black ER-180	Direct Black 38
Phenamine Black ER-200	Direct Black 38
Phenamine Dark Green B	Direct Green 1
Fastusol Brown LBRS	Direct Brown 95
Fastusol Brown LBRS 200	Direct Brown 95
Phenamine Brown MN	Direct Brown 2
Phenamine Brown MB 150	Direct Brown 2
Phenamine Fast Brown T	Direct Brown 31
Phenamine Fast Brown TSL	Direct Brown 31
Phenamine Brown D3G Conc.	Direct Brown 1A
Phenamine Black RW	Direct Black 4
Phenamine Black MP 200	Direct Black 38
Dressing Black SS	Acid Black 29

G A F CORPORATION

DYES CONTAINING BENZIDINE DYES:

Phenazo Brown RS
Direct Brown YY 133
Penetrating Black AL
Chrome Leather Brown HS
Suede Black AKC
Penetrating Black FS
Nyliton Fast Black AW
Fastusol Brown TM
Fastusol Blue PF
Fastusol Brown BRLU
Union Olive Green 408 NC New
Union Olive Green 408 IDF
Union Govt Black I
Phenamine Black ERH
Phenamine Black LB
Suede Leather Black WM
Suede Leather Black WMR
Phenamine Black GAC
Phenamine Brown SB
Phenamine Brilliant Blue BBR New
Chrome Fast Orange 3RLA
Union Government Black
Chrome Leather Blacked
Acid Black Brown BA
Nyliton Fast Black DSR
Fastusol Grey LRS
Fastusol Fast Brown RLS
Fastusol Brown BRL
Aniline SAP Brown DGS
Phenamine Brown TC
Phenamine Dark Brown NZ
Leather Black FL
Phenamine Black Dy-200
Phenamine Dark Green H
Suede Leather Black WMB
Phenamine Fast Brown TG
Phenamine Red DB
Phenamine Black ERB

ALLIED CHEMICAL

BENZIDINE DYES

Erie Green GPD
Erie Green MT
Erie Green WT

Erie Fast Orange G
Erie Orange 2R
Milling Orange R

Milling Scarlet G
Erie Bordeaux B
Erie Congo 4B
Erie Fast Red FD
Erie Scarlet B
Erie Congo 4BP

Diazine Black HX
Erie Black HS
Erie Black GPNF
Erie Black GXR
Erie Black GXOO
Erie Black NUG
Diazine Black HP

Niagara Blue 2B
Niagara Blue 2BC

Erie Brown 3GN
Erie Catechine 3G
Erie Fast Brown B
Erie Fast Brown 3RB
Solantine Brown BRL
Solantine Brown BRLP

ALLIED CHEMICAL

BENZIDINE-BASED DYE MIXES

Acid Brown TM
Milling Scarlet 2BNH
Naccoprint Scarlet HCH
Acid Violet TWP
Bottom Black ADS
Bottom Black 23189
Leather Black BPT
Patent Black 36543
Penetrating Black KN
Suede Black ABK
Penetrating Black PV
Erie Black NXG
Erie Black BP
Para Black RRM New
Para Black MHC
Para Black MCC
Leather Black BLN
Direct Brown BNS
Leather Brown AKW
Direct Khaki US
Direct Khaki US 90%
Nacco Brown GG-BU
Nacco Brown GG 90%
Padding Brown HVL
Erie Catechine G-Q818
Direct Brown NRL
Erie Brown S-5617
Direct Brown L-53901
Leather Dark Brown GAK
Direct Tan E-46774
Direct Brown D-33484
Direct Brown K-74462
Nat'l Leather Brown CL-138
Direct Brown MH
Ramil Brown JAD
Paper Brown RP
Penetrating Black A
Wool Black S-10565-C
Erie Black 5R
Direct Black KF
Penetrating Black MSB
Direct Buff 9611
Seal Brown CF
Florist Green A 99529
Red Shop Towel Dye
Leather Black MFT

Direct Black FPC
Latex Tan ATG
Erie Fast Black SHG 150%
Erie Black RCC
Leather Blue Black MOS
Nat'l Direct Blue 2BR
Direct Seal Brown 41855
Direct Brown S-10519-1
Leather Black 19847 New
Direct Blue TF
Erie Brown GGRD
Bottom Brown GL-103
Direct Grey C-13141
Erie Brilliant Brown S-9489
Erie Fast Brown B-S
Direct Brown C-12876
PF Direct Brown WEN
Direct Garnet C-11678
Seal Brown NBS
Leather Tan STC
Acid Brown R-63739
Alum. Dark Brown 53109
Direct Brown K 74462
Direct Brown MH
Erie Fast Brown GRS
Leather Dark Olive ASB
Ramile Light Olive DCS
Direct Catechine S-9329
Leather Brown ST
Sandal Glove MWL
Aluminum Brown PMC
Direct Printing Brown TH
Direct Brown 3R
Acid Grey AMT
Special Black RAM
Acid Grey AMTH
Resorcine Brown 3RN
Resorcine Brown DK
Direct Brown S-10519-1
Direct Brown D 33484
Leather Brown FLC
Nat'l Leather Brown BP
Erie Green MAT C-12672
Direct Paper Green GPD
Erie Fast Scarlet 4BSN

APPENDIX

D

CORRESPONDENCE OF GAF & ALLIED CHEMICAL CORPORATION TO CLIENTS REGARDING OXIDATIVE/REDUCTIVE STRIPPING PROCEDURES

GAF Corp.

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Dear Mr. Customer:

A number of important and useful GAF dyes use benzidine as a raw material. (see attached list). Our records show that your company purchases certain of these dyes. We have become aware of a possible environmental problem that could result from the use of such benzidine based dyes in a previously unforeseen way under certain processing conditions.

The possible environmental hazard with which we are concerned is associated with stripping, where this is required, and, in particular, where reductive stripping agents are used, such as sodium hydrosulfite. It has been observed that benzidine-based dyes may undergo chemical reaction in the presence of strong reducing agents to regenerate benzidine. In the course of a normal stripping operation the benzidine so formed may then become a component of the waste water discharged from the process.

While no specific U.S. Environmental Protection Agency regulation has yet been issued governing the discharge of benzidine into wastewaters, we have been advised that such a regulation is under consideration.

Accordingly, it is recommended that no reductive stripping be performed by the dyer. Rather, when stripping is required, oxidative stripping should be employed, e.g. using sodium hypochlorite. Information on this mode of stripping, including methods to minimize the necessity of stripping, will be supplied by GAF Corporation technical service on request at _______________.

We would appreciate your bringing this information to the attention of appropriate personnel in your organization. Should you have any questions on this matter, please contact me.

Very truly yours,

10/23

GAF Corp

DRUM LABEL:

PLEASE NOTE: If stripping is required oxidative stripping should be employed. Use of reductive stripping agents in treating materials dyed with this product may produce benzidine and should therefore be avoided.

G A F CORPORATION

BENZIDINE DYES

PRIMARY BENZIDINE DYES:

Phenazo Black BH	Direct Blue 2
Phenazo Black BH 50	Direct Blue 2
Phenazo Black BH 150	Direct Blue 2
Phenamine Blue BB Conc	Direct Blue 6
Phenamine Blue BBN	Direcet Blue 6
Supranol Red PG Extra	Acid Red 85
Supranol Red PRX	Acid Red
Paper Scarlet 3BP	Direct Red 39
Paper Scarlet BP	Direct Red 37
Phenamine Scarlet B	Direct Red 37
Phenamine Fast Red F	Direct Red 1
Paper Orange R	Direct Org 8
Phenamine Green G	Direct Green 6
Phenamine Green BG	Direct Green 6
Phenamine Black E	Direct Black 38
Phenamine Black E 200	Direct Black 38
Phenamine Black ER-180	Direct Black 38
Phenamine Black ER-200	Direct Black 38
Phenamine Dark Green B	Direct Green 1
Fastusol Brown LBRS	Direct Brown 95
Fastusol Brown LBRS 200	Direct Brown 95
Phenamine Brown MN	Direct Brown 2
Phenamine Brown MB 150	Direct Brown 2
Phenamine Fast Brown T	Direct Brown 31
Phenamine Fast Brown TSL	Direct Brown 31
Phenamine Brown D3G Conc.	Direct Brown 1A
Phenamine Black RW	Direct Black 4
Phenamine Black MP 200	Direct Black 38
Dressing Black SS	Acid Black 29

DYES CONTAINING BENZIDINE DYES:

Phenazo Brown RS
Direct Brown YY 133
Penetrating Black AL
Chrome Leather Brown HS
Suede Black AKC
Penetrating Black FS
Nyliton Fast Black AW
Fastusol Brown TM
Fastusol Blue PF
Fastusol Brown BRLU
Union Olive Green 408 NC New
Union Olive Green 408 IDF
Union Govt Black I
Phenamine Black ERH
Phenamine Black LB
Suede Leather Black WM
Suede Leather Black WMR
Phenamine Black GAC
Phenamine Brown SB
Phenamine Brilliant Blue BBR New
Chrome Fast Orange 3RLA
Union Government Black
Chrome Leather Blacked
Acid Black Brown BA
Nyliton Fast Black DSR
Fastusol Grey LRS
Fastusol Fast Brown RLS
Fastusol Brown BRL
Aniline SAP Brown DGS
Phenamine Brown TC
Phenamine Dark Brown NZ
Leather Black FL
Phenamine Black Dy-200
Phenamine Dark Green H
Suede Leather Black WMB
Phenamine Fast Brown TG
Phenamine Red DB
Phenamine Black ERB

GAF Corp.
Rensselaer Plant
10/27/75

PRODUCTS DERIVED FROM BENZIDINE

Code No.	Product Name
1-2-24119	Phenazo Black BH
1-2-21689	Supranol Red PG
1-2-14682	Paper Scarlet 3BP
1-2-14680	Paper Scarlet BP
1-2-14647	Phenamine Scarlet B
1-1-14646	Phenamine Fast Red F
1-2-14560	Paper Orange R
1-1-14430	Phenamine Green G
1-1-14419	Phenamine Green BG
1-2-14405	Phenamine Dark Green B
1-3-14340	Fastusol Brown LBRS
1-2-14319	Phenamine Brown MB
1-1-14331	Phenamine Fast Brown T
1-1-14302	Phenamine Brown D3G
1-1-14144	Phenamine Black RW
1-3-14122	Phenamine Black E
1-2-14115	Phenamine Black MP
1-1-14101	Phenamine Black ER
1-1-14187	Union Government Black
1-1-11150	Dressing Black SS

Allied
Chemical

Specialty Chemicals Division
P.O. Box 1087R
Morristown, New Jersey 07960

November 10, 1975

Our records show that your company purchases dyes containing benzidine-based material (see attached list) from Allied Chemical. We have become aware of a possible environmental problem that could result from the use of such benzidine-based dyes in a previously unforeseen way under certain processing conditions. The possible environmental hazard with which we are concerned is the use of these dyes with reductive stripping agents, e.g., sodium hydrosulfite or similar reducing agent, where this is required. It has come to our attention that benzidine-based dyes may be chemically reduced to benzidine when such dyes come into contact with strong reducing agents. This benzidine may then become a part of the wastewater discharged into your receiving waters.

While no specific U.S. Environmental Protection Agency regulation has yet been issued governing the discharge of benzidine into wastewaters, we have been advised that such a regulation is being considered.

Thus, it is recommended that no reductive stripping be performed by the dyer. Rather, when stripping is required, oxidative stripping should be employed, e.g., using sodium hypochlorite. Our recommended procedure for oxidative stripping is attached.

We would appreciate your bringing this information to the attention of appropriate personnel in your organization. Should you have any questions on this matter, please contact me at the above address or call me on 201-455-2154.

Very truly yours,

C. H. Vance

C. H. Vance
Manager, Technical Service
Dyestuffs and Intermediates

Attachments

ALLIED CHEMICAL

BENZIDINE DYES

Erie Green GPD
Erie Green MT
Erie Green WT

Erie Fast Orange G
Erie Orange 2R
Milling Orange R

Milling Scarlet G
Erie Bordeaux B
Erie Congo 4B
Erie Fast Red FD
Erie Scarlet B
Erie Congo 4BP

Diazine Black HX
Erie Black HS
Erie Black GPNF
Erie Black GXR
Erie Black GXOO
Erie Black NUG
Diazine Black HP

Niagara Blue 2B
Niagara Blue 2BC

Erie Brown 3GN
Erie Catechine 3G
Erie Fast Brown B
Erie Fast Brown 3RB
Solantine Brown BRL
Solantine Brown BRLP

ALLIED CHEMICAL

BENZIDINE-BASED DYE MIXES

Acid Brown TM
Milling Scarlet 2BNH
Naccoprint Scarlet HCH
Acid Violet TWP
Bottom Black ADS
Bottom Black 23189
Leather Black BPT
Patent Black 36543
Penetrating Black KN
Suede Black ABK
Penetrating Black PV
Erie Black NXG
Erie Black BP
Para Black RRM New
Para Black MHC
Para Black MCC
Leather Black BLN
Direct Brown BNS
Leather Brown AKW
Direct Khaki US
Direct Khaki US 90%
Nacco Brown GG-BU
Nacco Brown GG 90%
Padding Brown HVL
Erie Catechine G-Q818
Direct Brown NRL
Erie Brown S-5617
Direct Brown L-53901
Leather Dark Brown GAK
Direct Tan E-46774
Direct Brown D-33484
Direct Brown K-74462
Nat'l Leather Brown CL-138
Direct Brown MH
Ramil Brown JAD
Paper Brown RP
Penetrating Black A
Wool Black S-10565-C
Erie Black 5R
Direct Black KF
Penetrating Black MSB
Direct Buff 9611
Seal Brown CF
Florist Green A 99529
Red Shop Towel Dye
Leather Black MFT
Direct Black FPC
Latex Tan ATG
Erie Fast Black SHG 150%
Erie Black RCC
Leather Blue Black MOS
Nat'l Direct Blue 2BR
Direct Seal Brown 41855
Direct Brown S-10519-1
Leather Black 19847 New
Direct Blue TF
Erie Brown GGRD
Bottom Brown GL-103
Direct Grey C-13141
Erie Brilliant Brown S-9489
Erie Fast Brown B-S
Direct Brown C-12876
PF Direct Brown WEN
Direct Garnet C-11678
Seal Brown NBS
Leather Tan STC
Acid Brown R-63739
Alum. Dark Brown 53109
Direct Brown K 74462
Direct Brown MH
Erie Fast Brown GRS
Leather Dark Olive ASB
Ramile Light Olive DCS
Direct Catechine S-9329
Leather Brown ST
Sandal Glove MWL
Aluminum Brown PMC
Direct Printing Brown TH
Direct Brown 3R
Acid Grey AMT
Special Black RAM
Acid Grey AMTH
Resorcine Brown 3RN
Resorcine Brown DK
Direct Brown S-10519-1
Direct Brown D 33484
Leather Brown FLC
Nat'l Leather Brown BP
Erie Green MAT C-12672
Direct Paper Green GPD
Erie Fast Scarlet 4BSN

11/10/75

OXIDATIVE STRIPPING OF DIRECT, BENZIDINE DERIVED DYES FROM DYED MATERIALS

The dyed material is rewet in a hot bath containing 1% O.W.F. of soda ash and the amount of anionic wetting agent normally used for wetting.

Rinse clear of excess dye washed out of material.
Draw a fresh bath at 80° F.
Add a suitable chlorine compound.
Run 30 minutes at 80° F.
Raise to 120° F. and run 20 minutes.
Add 1% O.W.F. Acetic Acid 56%.
Run 20 minutes.
Rinse two times in fresh baths at 120° to 140° F.
Draw a fresh bath at 80° F.
Add sodium bisulfite at a concentration of 0.500 grams per liter.
Rinse in a fresh bath at 80° F.
Draw a fresh bath for redyeing the material.

Note:

Two generally used commercially available chlorine compounds are:

1. "HTH" a dry granular calcium hypochlorite containing 70% available chlorine.
2. Liquid Chlorine Bleach - a solution of sodium hypochlorite containing from 12% to 15% available chlorine.

For maximum stripping of most direct dyed shades, a concentration of about 0.15% available chlorine is needed in bath.

Use 2 grams per liter of HTH
or
12 grams per liter of Liquid Chlorine Bleach.

Some shades can be stripped with lesser amounts of available chlorine and some shades may require up to:

3 grams per liter of HTH
or
12 grams per liter of Liquid Chlorine Bleach.

Some modifications of this procedure may be required to accommodate variations in equipment and operating procedures.